SYNTHESIS AND CHARACTERIZATION OF ZIRCONIA BASED PYROCHLORES AND FUNCTIONALLY GRADED THERMAL BARRIER COATINGS

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ABSTRACT

8% yttria stabilized zirconia (8YSZ) thermal barrier coatings (TBCs) are current state-of-the-art material (in aerospace) to provide vital thermal protection to any metal component to serve continuously in environments operating at ~1150°C (maximum 1200°C). Typical TBCs (250µm up to 2 mm thick), lower metal temperature up to 150°C than the service temperature, allow longer life of the components. 8YSZ suffers from (a) poor adhesion and (b) phase de-stabilization at >1150°C. Hence superior materials are needed to replace 8YSZ with higher thermal fatigue life and characteristics to perform at >1150°C.

TBCs were plasma spray coated (APS) by using (a) novel TBC configurations and (b) newer ceramic TBC materials. This was carried out via (a) Functionally Graded Material (FGM) TBC configurations, by using conventional 8YSZ and by (b) development of novel zirconia based pyrochlores. The FGM concept was integrated with conventional 8YSZ and newer TBC materials (pyrochlores) for further enhancement. Conventional 8YSZ (METCO 205 NS) and NiCrAlY bond coat (AMDRY 962) spray powders were used for depositing TBCs on Inconel 718/ stainless steel and used for bench marking.

FGMs include a third intermediate layer made from blend of top coat and bond coat spray powders to minimize the thermal expansion mismatch at elevated temperatures. TBCs in FGM configurations were prepared from 3 different blends of plasma spray powders of NiCrAlY and 8YSZ (e.g 25%NiCrAlY + 75% 8YSZ). Characterization included (i) thermal fatigue tests between 1150 &1400°C by using (a) gas flame and (b) furnace, (ii) oxidation stability tests (at 800°C, 1000°C and 1150°C) and (iii) adhesion test (ASTM C633 standard), (iv) phase (XRD) and (v) micro structure (SEM/EDS) analysis in polished metallographic cross section.

The newer alternate TBC materials were Rare-Earth Zirconate Pyrochlores ($RE_2Zr_2O_7$, RE = rare earths, RE= La, Ce singly and in combination). Plasma spray powders of (i) Lanthanum Zirconate ($La_2Zr_2O_7$) (ii) Lanthanum Cerium Zirconate ($La_2 (Zr_{0.7}Ce_{0.3})_2O_7$ and (iii) Lanthanum Cerate ($La_2Ce_2O_7$) were synthesized via solid-state method and spray coated by APS method by using 3 different spray parameters (characterized similar to FGM TBCs).

FGM with Conventional 8YSZ TBCs (three layered system) in 50% NiCrAlY + 50% 8YSZ configuration exhibited superior thermal fatigue (life) (up to1400°C) over conventional 8YSZ (up to1000°C) TBCs. The exhaustive set of results pertaining to conventional duplex layer, FGM and multilayer configurations (with pyrochlore), improvement over conventional 8YSZ at 1200 and 1400°C forms the main body of this research which was complimented with limited studies on (i) residual stress analysis and (ii) thermal barrier effects (at 1000°C)

Key words: Thermal barrier coating, functionally graded material, zirconia based pyrochlore.

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1. INTRODUCTION

Thermal Barrier Coatings (TBCs) have found extensive use in aerospace applications since the fifties: however, research work continues with specific goals to find newer and innovative improved materials for various applications, configurations, characterization methods etc. The main purpose of TBCs is to reduce the surface temperatures of metal components on which they are applied and which are subjected to high temperature (1000˚C and above depending upon application) in service [1][2]. This is required to improve the life of the underlying metal components by providing protection from the harshness of the high temperature environment including oxidation, corrosion and prevent failure etc. To increase the in-service performance temperature of the base metal (typically high temperature super alloys), thermal insulating material (in the form of coatings) having very low thermal conductivity and associated characteristics are required [3]. A typical TBC system comprises of duplex layer i.e., the substrate followed by the bond coat (BC) layer (~75μm) and over that a suitable ceramic top coat (TC) layer (~250μm to 2mm). Schematic of TBC system as shown in figure 1. The coatings are typically applied by two methods: (1) Electron-beam physical vapor deposition EBPVD and (2) Atmospheric plasma spraying (APS): the former although a high-quality coating system, is extremely expensive. Thus, APS coating systems are widely used worldwide for R & D purposes. The top ceramic layer and the base metallic layer have unequal coefficients of thermal expansion (CTE). The BC is therefore necessary to reduce corrosion, to improve bonding, and even out the differences (in expansion) between the ceramic and base metallic substrate layers.

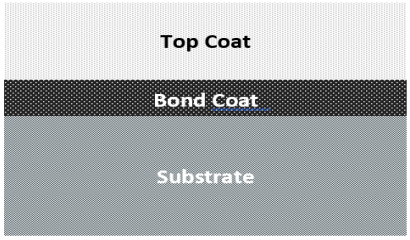


Figure 1. Schematic of TBC system

Currently, the most commonly used TBC material is 7-8 weight percent of Yttria Stabilized Zirconia (YSZ) which has found wide application in aerospace components (gas turbines) as the standard top coat TBC material (protective over layer) [2]. This is due to its ability to withstand temperatures of up to 1150˚C without spallation in service: which involves thermal shock and other thermal stresses related damage. 8YSZ can successfully decrease the surface temperature of the substrate material to a more tolerable range which is attributable to its thermal barrier effect due to low thermal conductivity properties [4]. However, due to the continuous thermal cyclic stresses generated during service, the TBC system undergoes failure (cracks and / or spallation. One of the key reasons for this is the coefficient of thermal expansion (CTE)

mismatch at higher temperatures (1000-1200^{o}C). YSZ, a stable form of tetragonal-ZrO_2 or cubic-ZrO_2 undergoes destabilization to (m) monoclinic-ZrO_2 when subjected to >1200^{o}C associated with 3–5% volume expansion upon cooling. Due to the expansion characteristics, the specimen tends to fail or spall. Furthermore, the YSZ layers are also likely to sinter at T > 1200^{o}C, which increases the thermal conductivity of the ceramic topcoat (TC) [8]. Thermal stress and strain tolerance can be reduced through sintering and densification of the TC which can significantly reduce the coating's durability in service. To circumvent this issue, the concept of functionally graded materials (FGMs) has been explored. FGM materials are a mixture of the bond coat (BC) and ceramic top coat (TC) plasma spray powders in varying ratios (as shown in figure 2): which as intermediate coatings play important role of a middle layer that minimizes the CTE mismatch at elevated temperatures [10]. This helps to reduce the thermal expansion mismatch as the FGM layer is assumed to have thermal properties in between the two layers (bond and ceramic top coat).

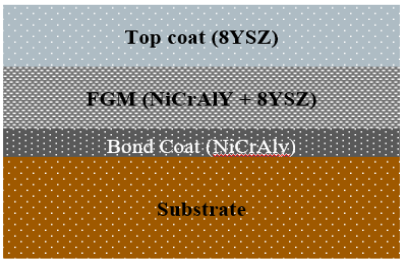


Figure 2. Schematic of FGM TBC system

To further increase the operating temperatures of turbine engines, alternate TBC materials with low thermal coefficient, higher thermal stability and superior sintering resistance are required [6][7]. Improved TBC characteristics in zirconia base TBC material are also likely to be achieved by using novel ceramic materials. Pyrochlore of general composition, $A_2B_2O_7$ are used to develop TBCs with properties superior to 8YSZ [11]. Low-Thermal-Conductivity Rare-Earth Zirconate Pyrochlore - type system ($RE_2Zr_2O_7$, RE = rare earths such as La, Sm, Ce, Dy, Gd, etc.) have good potential for TBCs applications. In addition to low thermal coefficient and in contrast to the phase transformation the currently popular YSZ-TBCs undergoes at ~1200^{0}C, the RE Zirconate Pyrochlore TBCs exhibit very good phase stability at these and higher temperatures [11]. For applications involving TBCs, the goal is to develop Rare-Earth Zirconate Pyrochlore based coatings which promise improved high temperature properties (>1200°C). These TBCs are expected to allow increased gas turbine efficiencies that will function effectively at higher than the current operating temperatures [12]. However, adhesion of the pyrochlore coatings to the bond coated substrates has been reported to be a cause for concern. Pyrochlore coatings in combination with YSZ and intermediary layer or in FGM configuration with NiCrAlY bond coat configuration is expected to perform in a superior manner.

2. LITERATURE REVIEW

The typical structure of thermal barrier coatings (TBCs) comprises of three layers (1) the substrate; (2) the bond coat and (3) the ceramic top coat. 8YSZ can successfully reduce the surface temperature of the substrate material to a more tolerable range which is attributable to its thermal barrier effect due to its high thermal insulating properties [2]. However, due to the continuous thermal cyclic stresses generated in service, the TBC system undergoes failure. One of the key reasons for this is the coefficient of thermal expansion mismatch and to circumvent this issue, the concept of Functionally Graded Materials (FGM) has been introduced [10]. FGM materials are a mixture of the bond coat (BC) and top coat (TC) plasma spray powders in varying ratios. This FGM layer is placed in between the bond coat (NiCrAlY) and top coat (8YSZ) that plays the role of an intermediate layer that minimizes the CTE mismatch at elevated temperatures [10]. Generally Atmospheric Plasma Spray (APS) coating is a popular method to apply the coatings.

To increase the in-service performance temperature of this metal, thermally insulating materials (in the form of coatings) having very low thermal conductivity are required. Currently, the most commonly used TBC material is 8YSZ which not only possesses low thermal conductivity (2.2 W/mK) but performs well (withstands thermo-mechanical stresses) efficiently [11]. In order to attain increased efficiency and durability, the present-day need is to increase the service temperatures >1200^{o}C by newer materials and configurations. This technological requirement warrants development of newer TBC materials with thermal conductivities lower than 8YSZ but without compromising on other materials characteristics such as thermal shock resistance, adhesion, microstructure etc.

One of the promising candidates for the TBCs is Pyrochlore-type rare earth zirconium oxides ($RE_2Zr_2O_7$, Re = rare earth). $RE_2Zr_2O_7$ TBCs have higher phase stability, lower thermal conductivity, lower sintering rate, no phase transformation, and lower coefficient of thermal expansion at elevated temperatures when compared with YSZ [6]. Zirconia based materials/coatings with pyrochlore structures (a derivative of fluorite) have shown high potential as a TBC to serve at 1400^{o}C, due to their favourable thermal insulating characteristics [7]. In addition to thermal and structural characteristics, adhesion strength of the TBC with the substrate/ component also is an important property to be studied to find a suitable replacement to 8YSZ. Therefore, many configurations involving suitable combinations of different ceramic layers (8YSZ and pyrochlore composites) are also being widely researched.

The table below depicting information is related to recent research findings in the area of FGM and pyrochlore TBCs their applications and significant research gaps

X.Q. Cao et al. [4] Ceramic materials for thermal barrier coatings. Journal of the European Ceramic Society (2004)
Summarizes the basic properties of ceramic materials for TBCs. Ceramics, in contrast to metals, are often more resistant to oxidation, corrosion and wear, as well as being better thermal insulators. Except yttria stabilized zirconia, other materials such as lanthanum zirconate and rare earth oxides are also promising materials for TBCs.
Brian Gleeson et al. [13] Thermal Barrier Coatings for Aeroengine Applications. Journal of Propulsion and Power (2006).
Newer mechanisms that governs TBC performance have been brought out. TBCs advances will be in the areas of 1) new bond coat compositions which meet higher metal temperature capabilities; 2) low thermal conductivity ceramic topcoats with improved resistance to extrinsic degradation mechanisms, such as erosion and calcium magnesium alumino-silicate (CMAS) attack; 3) improved life-prediction models that account for time and temperature-dependency and 4) the more effective use of sensors and nondestructive evaluation methods for assessing remaining TBC life.
K.A.Khor et al. [14] Plasma sprayed functionally graded thermal barrier coatings. Materials Letters (1999)
Five-layered FGM coatings were fabricated using three different composite powders with compositions (1) 75% NiCoCrAlY:25% YSZ; (2) 50% NiCoCrAly:50% YSZ and (3) 25% NiCoCrAlY:75% YSZ. These composite powders can assist to obtain homogeneous coating structures in each inter-layer. The unique microstructure feature and good mechanical properties achieved would provide extended service life for the FGM thermal barrier coating.
Y.W. Gu et al [15] Functionally graded ZrO_2-NiCrA1Y coatings prepared by plasma spraying using pre-mixed, spheroidized powders. Surface and Coatings Technology (1997)
Pre-mixed powders were used post-mechanical milling and plasma spheroidizing as a raw material to produce the ZrO_2-NiCrAlY coatings. Here Nickel stubs and Aluminum plates were used as substrates, whereas three different types coatings were prepared; (i) duplex coatings of NiCrAlY and ZrO_2, (ii) ZrO_2-NiCrAlY with various layers coating, and (iii) peel-off coatings to determine properties of different layers. The microstructure analysis involved characterizing the morphology of different features in the coating's layers and the fracture modes. From the bond strength measurements, the strength was observed to be increasing with the number of graded layers i.e. FGM TBCs were stronger in their bonding with the substrate. .
Klod Kokini et al. [16]. Thermal shock of functionally graded thermal barrier coatings with similar thermal resistance, Surface and Coatings Technology (2002)

Thermal fatigue in functionally gradient TBCs was found to be a major cause for the failure of the single layer TBC due to the unequal expansion coefficient between the ceramic and the metal substrate. To reduce the above difficulty, it was reported that dividing the top coat into finite number of layers and each layer having a gradient mixture of the both the ceramic and the metal at different percentages. After the thermal shock tests it was concluded that more the number of the layers, the more gradual the properties were in the transition.
Jing Zhang et al. [17]. Lanthanum zirconate based thermal barrier coatings: A review, Surface & Coatings Technology (2017)
Manufacturing methods of lanthanum zirconate ($La_2Zr_2O_7$, LZ) TBCs were reported. Lanthanum zirconate is a promising candidate material for TBC applications. LZ has lower thermal conductivity and higher thermal stability compared to conventional TBC systems. Summarised physical and meachanical properties of LZ. Thermal cycling behavior, durability and its performace is compared with conventional (YSZ).
Praveen K et al. [18]. Lanthanum cerate thermal barrier coatings generated from thermal plasma synthesized powders. Ceramic International (2018).
Several new ceramic materials including $Gd_2Zr_2O_7$, $La_2Zr_2O_7$ and $La_2Ce_2O_7$, have been investigated for their possible application as advanced TBC materials. Among the materials investigated, $La_2Ce_2O_7$ (LC) is a promising material for TBC applications. The thermal conductivity (0.5–1.02 W/m K at 1473K) of LC is much lower than that of YSZ (thermal conductivity of 2.1 W/m K). Further, the coefficient of thermal expansion of (12.3–12.6 x 10^{-6} /K at 573–1473K) of LC is higher than that of YSZ (10.5–11.5 x 10^{-6} / K).
Jing Zhang et al. [19]. Mechanical properties of lanthanum zirconate based composite thermal barrier coatings. Advances in Applied Ceramics Structural, Functional and Bio-ceramics (2019).
Mechanical properties of the new composite LZ/8YSZ TBC systems. Nickel-based superalloy (Nimonic 263) was used as the substrate. The mechanical properties of the as-sprayed TBC specimens were measured using both nanoindentation and microhardness tests. Multi-layered composite coatings were fabricated with varying composites in each layer. The 8YSZ and LZ were premixed with five different volume ratios: 0:100 (pure LZ), 25:75, 50:50, 75:25 and 100:0 (pure 8YSZ).
Guanlin Lyu et al. [20] Sintering behavior and phase transformation of YSZ-LZ composite coatings. Ceramic International (2020)
YSZ-LZ composite coatings were prepared by using the APS method. The system takes advantage of the thermal insulating property of LZ and the mechanical properties of YSZ. The phase stability and sintering behavior of the composite coatings were investigated using the isothermal exposure test at three different temperatures (1100, 1300, and 1400°C). X-ray diffraction (XRD) were used to analyze the influence of phase transformation. The sintering resistance and phase stability of the YSZ-LZ composite coatings were also discussed.

3. PROBLEM IDENTIFICATION & STATEMENT

The current state-of-the-art TBC material in commercial use is 8%yttria-stabilized zirconia, well known as 8YSZ. This material undergoes structural phase change at ~1170°C and above, which severely limits its suitability in applications involving service conditions higher than even 1100°C. Significant problems associated with 8YSZ are the following.

- Structural phase transformation: Above 1200°C, 8YSZ transforms from tetragonal and cubic phase and during cooling process it changes to monoclinic (m) phase with a volume expansion of about 3–5 vol.%, resulting in the spallation or delamination of TBCs
- Sintering effects: At T> 1200°C, 8YSZ layers are prone to sintering, which increases thermal conductivity and makes them less effective. Sintered and densified coatings increases the thermal stresses, reduce strain tolerance and decrease the coating's durability.
- Thermal expansion mismatch: Poor adhesion in the coatings are formed due to the thermal expansion mismatch between the ceramic and metal coating layers. Adhesion mismatch between a metal substrate and the ceramic result in adhesive failure and sometime inter-ceramic separation (cohesive failure).

This aspect must be addressed and may be circumvented by employing the functionally graded material (FGM) concept. FGM layers involve inclusion of third plasma spray coated layer between the bond and top coat synthesized from blends of two or three different plasma sprayable powder materials such as ceramic and bond coat in different proportions (to gradually bring about a change in coating characteristics). FGM TBCs are likely to possess improved spallation resistance which will be investigated in this research work.

To reduce the thermal mis-match strain a new concept of FGM, having gradual compositional variation over definable geometric orientations and distances is evolved. TBCs synthesized by using this new concept is expected to provide a gradual change in the thermal expansion characteristics and thus increase their thermal fatigue life

It is also very important to develop ceramic coatings which possess thermal conductivity lower than that of 8YSZ, and have reduced sintering effects in service at temperatures higher than 1100^0C. Newer materials such as pyrochlore structured zirconates with low thermal expansion, higher thermal stability and better sintering resistance must be investigated for TBCs as alternatives to 8YSZ.

To further increase the operating temperatures of turbine engines, without sintering and structural phase destabilization, alternative TBC materials (zirconia based pyrochlore) will be investigated in the present research

4. OBJECTIVES & METHODOLOGIES

The work proceeds with the following objectives.

1. To develop advanced TBCs with extended life over the conventional 8YSZ TBCs by employing coatings made from blends of bond coat and 8YSZ topcoat ceramic powders as intermediate layers in novel concept of Functionally Graded Materials (FGM).
2. To develop Rare-Earth Zirconate Pyrochlore based TBCs in duplex and FGM configuration to assess their capabilities to withstand higher operating temperatures (via thermal fatigue properties) up to 1400°C and to study the potential of their applications involving TBCs, as an alternative to the current state-of-the-art material 8YSZ.
3. To integrate the newly developed RE Zirconate Pyrochlore and FGM TBCs to increase the stability at T > 1200°C and up to 1400°C by newer (multilayer) coating configuration and compare over the conventional 8YSZ with a goal to further improvise the TBC characteristics.

The Methodology of the research work followed is shown in figure 3. Beginning from the preparation of pyrochlore compositions, preparation of plasma sprayable powders, coated test specimens through grit blasting followed by application of bond coat by APS, blend mix and top coat both in yttria stabilized zirconia FGM configuration and zirconia based pyrochlore, the entire exercise involved several tests at each stage which are the following.

- Adhesion of the coating systems measured using ASTM C633-13(2017) standard method.
- Thermal fatigue tests (at 1200^{o}C and 1400^{o}C) in laboratory scale basic gas flame test facility (Milder version of burner rig test (Practiced by NASA) and high temperature furnace (ASTM C 1171-16) standard method. The tests involved subjecting the TBCs to short duration thermal shock cycles by alternately exposing to high temperature at 1150^{0}C and ambient (forced air cooling) at room temperature.
- Oxidation stability test of all the TBCs at 800^{0}C-1150°C in a muffle furnace (Test performed based on NASA reports, exposure of the coatings for long duration at the high temperature)
- Structural phase analysis of the as-sprayed coated surface via X-ray Diffractometry (XRD).
- Microstructural analysis via Scanning Electron Microscopy (SEM) on polished metallographic cross section removed from spray coated samples ASTM B487–85(2013).

Further, the TBCs would undergo thermal barrier test and residual stress analysis to a limited scope of experiments. Thus the (a) FGM configurations, (b) zirconia based pyrochlore compositions, (c) plasma spray parameters, (d) thermal fatigue analysis, adhesion, structural phase and microstructural characterization, and finally (e) arrival at the best coating composition and configuration based on results obtained within the experimental framework of tests performed will be the main objective of the present research work.

Flow Chart of Research Methodology

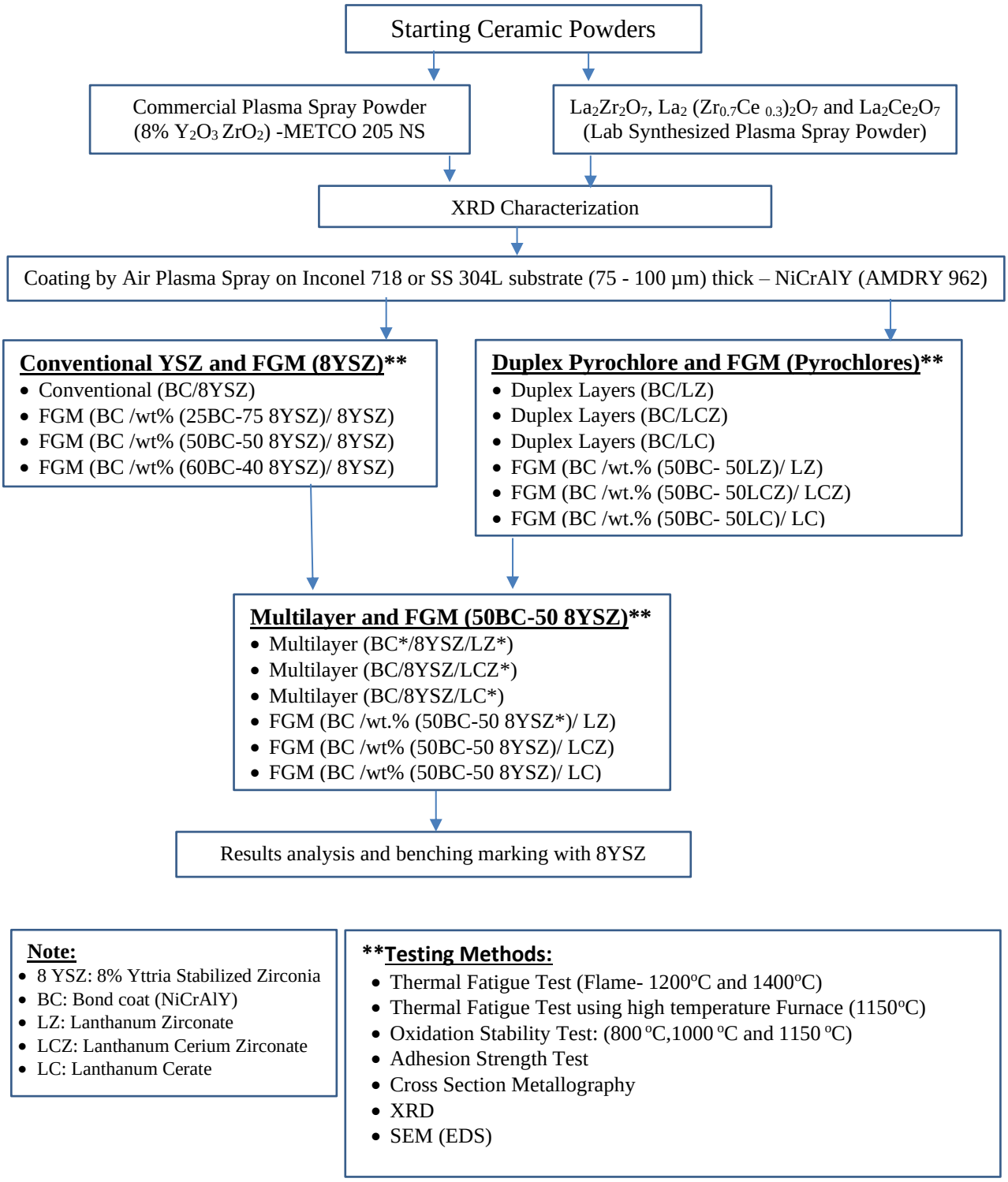

Starting Ceramic Powders
Commercial Plasma Spray Powder (8% Y_2O_3 ZrO_2) -METCO 205 NS
$La_2Zr_2O_7$, $La_2(Zr_{0.7}Ce_{0.3})_2O_7$ and $La_2Ce_2O_7$ (Lab Synthesized Plasma Spray Powder)
XRD Characterization
Coating by Air Plasma Spray on Inconel 718 or SS 304L substrate (75 - 100 µm) thick – NiCrAlY (AMDRY 962)
Conventional YSZ and FGM (8YSZ)**
Conventional (BC/8YSZ)
FGM (BC /wt% (25BC-75 8YSZ)/ 8YSZ)
FGM (BC /wt% (50BC-50 8YSZ)/ 8YSZ)
FGM (BC /wt% (60BC-40 8YSZ)/ 8YSZ)
Duplex Pyrochlore and FGM (Pyrochlores)**
Duplex Layers (BC/LZ)
Duplex Layers (BC/LCZ)
Duplex Layers (BC/LC)
FGM (BC /wt.% (50BC- 50LZ)/ LZ)
FGM (BC /wt.% (50BC- 50LCZ)/ LCZ)
FGM (BC /wt.% (50BC- 50LC)/ LC)
Multilayer and FGM (50BC-50 8YSZ)**
Multilayer (BC*/8YSZ/LZ*)
Multilayer (BC/8YSZ/LCZ*)
Multilayer (BC/8YSZ/LC*)
FGM (BC /wt.% (50BC-50 8YSZ*)/ LZ)
FGM (BC /wt% (50BC-50 8YSZ)/ LCZ)
FGM (BC /wt% (50BC-50 8YSZ)/ LC)
Results analysis and benching marking with 8YSZ
Note:
8 YSZ: 8% Yttria Stabilized Zirconia
BC: Bond coat (NiCrAlY)
LZ: Lanthanum Zirconate
LCZ: Lanthanum Cerium Zirconate
LC: Lanthanum Cerate
**Testing Methods:
Thermal Fatigue Test (Flame- 1200ºC and 1400ºC)
Thermal Fatigue Test using high temperature Furnace (1150ºC)
Oxidation Stability Test: (800 ºC,1000 ºC and 1150 ºC)
Adhesion Strength Test
Cross Section Metallography
XRD
SEM (EDS)

Figure 3. Methodology of Work

5. RESEARCH WORK ACCOMPLISHED

5.1. Experimental Methods

5.1.2 Powder Preparations & Materials

Commercial NiCrAlY (AMDRY 962) bond coat (BC), 8% Yttria stabilized zirconia (8YSZ) (METCO 204NS) and lab synthesized ceramic top coat pyrochlore plasma spray powders of (i) Lanthanum Zirconate ($La_2Zr_2O_7$): abbreviated as LZ (ii) Lanthanum Cerium Zirconate (La_2 ($Zr_{0.7}$ $Ce_{0.3}$)$_2O_7$: abbreviated as LCZ and (iii) Lanthanum Cerate ($La_2Ce_2O_7$): abbreviated as LC, were used as the starting materials. Nickel base super alloy (Inconel 718) and SS 304L were used as substrate of dimensions 80 mm x 80 mm x 5 mm (thickness) and 25 mm x 10 mm x 5 mm (thickness). Plasma-sprayed coatings were produced by atmospheric plasma spray (APS) method with a 100 Kw Sulzer METCO Sulzer. Bond coat (BC)- AMDRY 962 (Ni-22Cr- 10Al-1Y, -106 +52μm), METCO 204NS (8% Y_2O3-ZrO_2, -106+11 μm) and laboratory prepared plasma spray powder were used for plasma spray coating on the substrate.

5.1.3 TBCs Configuration Design

The specimen designations of TBC system used in this work are shown in Table.1.

TABLE 1. Specimen Designation

Sl. No	Specimens	Specimen Designation
1.	Conventional (BC/8YSZ)	Conv 8YSZ
2.	Duplex Layers (BC/LZ)	Duplex LZ
3.	Duplex Layers (BC/LCZ)	Duplex LCZ
4.	Duplex Layer (BC/LC)	Duplex LC
5.	FGM (BC /wt.% (25BC-75 8YSZ)/ 8YSZ)	FGM 1
6.	FGM (BC /wt.% (50BC-50 8YSZ)/ 8YSZ)	FGM 2
7.	FGM (BC /wt.% (60BC-40 8YSZ)/ 8YSZ)	FGM 3
8.	FGM (BC /wt.% (50BC-50LZ)/ LZ)	FGM 4
9.	FGM (BC /wt.% (50BC-50LCZ)/ LCZ)	FGM 5
10.	FGM (BC/ wt.% (50BC-50 50LC)/ LC)	FGM 6
11.	FGM (BC /wt.% (50BC-50 8YSZ)/ LZ)	FGM 7
12.	FGM (BC /wt.% (50BC-50 8YSZ)/ LCZ)	FGM 8
13.	FGM (BC/ wt.% (50BC-50 8YSZ/ LC)	FGM 9
14.	Multi-Layer (BC/YSZ/LZ)	M1
15.	Multi-Layer (BC/YSZ/LCZ)	M2
16.	Multi-Layer (BC/YSZ/LC)	M3

Ceramic Coatings in two configurations were prepared: (a) conventional TBC's which comprised of a bond coat (~ 75 micron thick) layer and top coat layer (250 to 300 micron thick TC layer) on the substrate (b) FGM consisting of three layers over the substrate (bond coat (~ 75 micron thick), (bond coat –top coat blend-(~ 100 to 150 micron thick)) and finally the top coat (~ 100 to 150 micron thick) overlay). Prior to deposition on the metal substrate, the specimens were grit blasted with alumina followed by plasma spray coating in conventional and FGM configurations. Three different spray parameters were used to coat the pyrochlores and the parameters that gave the best results are shown in Table 2.

TABLE 2. Plasma Spray Coating Parameters

Plasma Spray Parameters (P)	NiCrAlY (Bond Coat)	8YSZ(Top Coat)	LZ/LCZ/LC (Top Coat)
Voltage (V)	75	70	60
Current (A)	400	550	400
Power (kW)	24	35	24
Primary gas, Ar (SLPM)	57	38	14
Secondary gas, H_2 (SLPM)	17	19	5
Power feed rate (g/min)	45	35	10
Spray distance (mm)	100	100	100

5.1.2 Thermal Fatigue Tests by Using Gas Flame:

Thermal fatigue resistance is a very important factor deciding the life of the TBC. Thermal fatigue tests were carried out at 1200^{o}C and 1400^{o}C. In order to measure the thermal shock resistance of the coatings, the ceramic surface was heated to a pre-defined high temperature for 60 seconds (one minute) and the oxyacetylene gas flame was removed, and ceramic surface was force cooled with air for 60 seconds (one minute).This completed one cycle which induces a thermal strain in the TBC system. The failure typically occurs due to the presence of residual thermo-mechanical stresses generated in the TBC system. These stresses are caused due to the difference in coefficient of thermal expansion (CTE) mismatch between the ceramic top coat (TC) and the metallic bond coat (BC) or in some cases between the BC and the substrate.

5.1.4 Thermal Fatigue Test in High Temperature Furnace

In thermal fatigue evaluation, the specimens that were coated on all surfaces underwent thermal fatigue cycle tests. The test comprised of placing the specimen inside the muffle furnace, maintained @ 1150^{o}C, hold for 2 minutes @ 1150^{o}C before air quenching (fan cooling) in laboratory ambient (Room temperature @~25^{o}C). The end of a 2-minute cool cycle completed one thermal shock cycle. The tests were carried out based on the guidelines of the standard ASTM C 1171-16 and the goal was to determine which of the coated composition could withstand the most number of cycles without cracking or peeling away of the ceramic coatings.

It is important to note that the coated samples were introduced in the high temperature furnace 1150^{o}Cand removed at the same temperature after hold time. After a certain number of cycles were completed, the specimen was taken off the furnace muffle, subjected to visual inspection for failure/detachment of coating and reintroduced into furnace. The cycles were repeated till coatings failed.

5.1.3 Oxidation Stability Test

Oxidation stability of the coated system plays a vital role to determine its thermo-mechanical behaviour and thus to estimate the life of the ceramic coat when subjected to high temperature environment. To study the isothermal cyclic oxidation behaviours and microstructure changes of conventional TBC and different FGM composition, completely coated all sides of the substrate were covered with TBC. The tests were performed by introducing the samples in a furnace at room temperature, raising to three different temperatures separately (800℃,1000℃ and 1150℃), holding at the desired high temperature for 12 hours, followed by cooling inside the furnace for 12 hours to room temperature. The specimen was removed, visually inspected for defects, before repeating the cycle, until the coating showed signs of cracking or peeling off.

5.1.5 Adhesion Strength Test

Adhesive bonding may involve different mechanisms that occur simultaneously during the coating process, with varying parameters. The most important one in the process of APS is the joint formed due to substrate surface roughness. The adhesion of the coating is dependent on surface cleaning of the substrate, grit blasting methodologies, coating parameters and surrounding and the test was carried out by following the ASTM-C633 (2017) standard [9].

5.1.4 Material Characterization

Analyses of the crystallographic structural phases of the raw and plasma spray powders were carried out by using (XRD). Cross-section metallographic sections of as-sprayed coated specimen of thermal shock and oxidation stability tested specimens, were also analysed using SEM using ASTM B487 – 85 (2013) standard.

6. RESULTS AND DISCUSSION

6.1 Microstructure of As-sprayed Coatings - 8YSZ and FGM (typical)

Figure 4 shows the microstructures of as sprayed coatings of (a) Conventional 8YSZ (b) FGM 2 (typical) TBCs when studied in polished metallographic cross section.

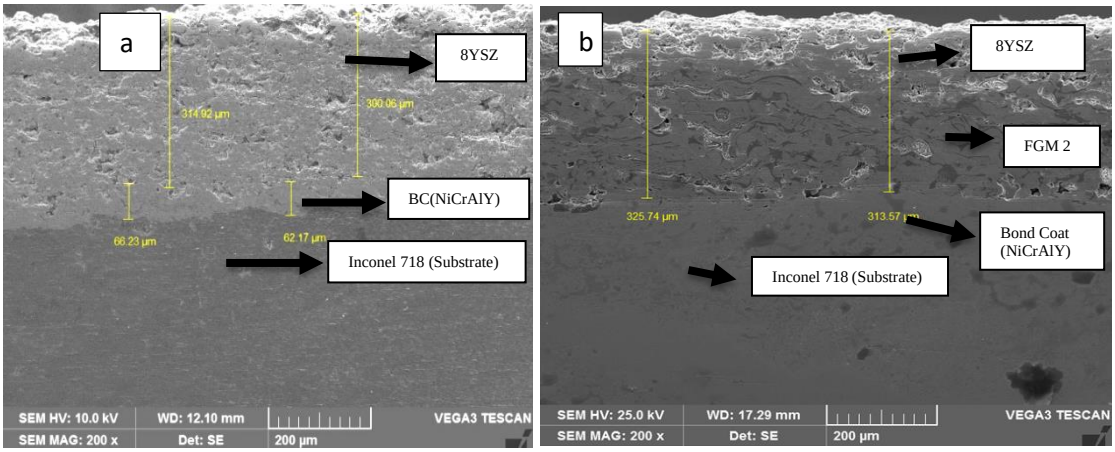


Figure 4. SEM image of typical As-sprayed cross-sectioned specimen: (a) Conventional 8YSZ (b) FGM 2

6.2 SEM (EDS) and XRD analysis of LZ

EDS with SEM was used to analyse the chemical composition of the processed powders and TBCs. Typical results on LZ TBC. Lanthanum (La), Zirconium (Zr) and oxygen (O) were present, confirming the most likely composition to be Lanthanum Zirconate which was confirmed via XRD. XRD patterns of raw mix (La_2O_3+ ZrO_2), LZ calcined powder (1150^{o}C and 1500^{o}C) are shown in Figure 5 (a to c).

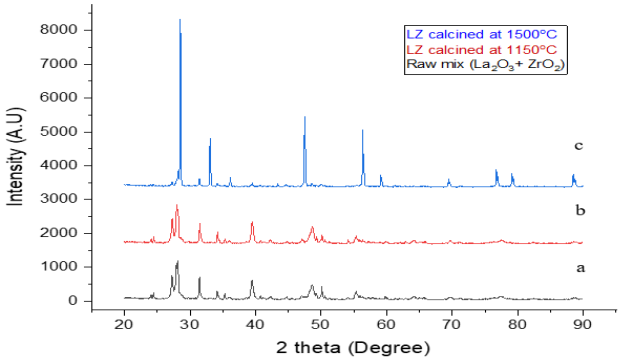


Figure 5. XRD patterns of (a) raw mix (La_2O_3+ ZrO_2); (b) LZ calcined at 1150^{o}C; (c) LZ calcined at 1500^{o}C

XRD patterns shown in Fig. 5a, as expected showed the peaks pertaining to La_2O_3 and m-ZrO_2, the raw mix powder compositions. To obtain the compound, i.e. LZ, the raw mix powders were calcined at two temperatures i.e.1150 and 1500^o C and the patterns are shown in Fig. 5(b, c). While the initiation of compound formation was depicted by the XRD pattern for the mix calcined at 1150^o C, complete Lanthanum Zirconate (LZ) phase was formed when the calcination temperature was 1500^{o}C. Peaks pertaining to La_2O_3 and m-ZrO_2 phase present in Figure 5a, and 5b, disappeared in Figure c, indicating that phase formation of LZ was complete.

6.3 Thermal Fatigue test using oxyacetylene flame on conventional 8YSZ and FGM TBCs

The results pertain to the thermal fatigue test when the hot face (ceramic surface) was subjected to flame temperature at ceramic surface at 1200°C and 1400°C. The conventional 8YSZ specimen when exposed to 1200°C and 1400°C (separate tests) failed at the end of 158 and 35 thermal shock cycles respectively as shown in Fig. 6 (a, b), while the specimen with FGM 2 withstood more than 273 cycles without failure at 1200°C and also at 184 cycles when exposed to 1400°C. Failure was recorded when the topmost ceramic layer (visible to naked eye) either cracked or showed signs of delamination as shown in Fig. 6 (a, b c and d).

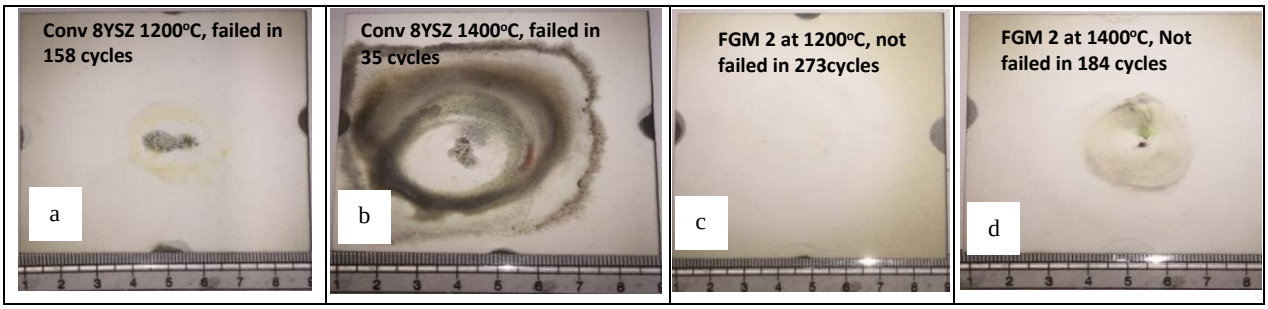

Conv 8YSZ 1200°C, failed in 158 cycles
a
Conv 8YSZ 1400°C, failed in 35 cycles
b
FGM 2 at 1200°C, not failed in 273cycles
c
FGM 2 at 1400°C, Not failed in 184 cycles
d

Figure 6 (a thru d): Surface of typical conventional 8YSZ and FGM 2 TBCs, thermal fatigue tested at 1200°C and 1400°C

From these results it may be concluded that an introduction of FGM layer plays an important role in determining the life of coatings under the thermal shock cycles test conditions adopted in this work. The highly superior characteristics of the coatings in the FGM configurations in TBCs were established through the above experiments. Plasma spray coatings carried out in 3 different spray facilities (manual and robotic gun controls) gave results highly similar to each other thereby confirming the authenticity of findings. Table 3 shows a typical thermal fatigue test results by using gas flame at 1200°C and 1400 °C.

TABLE 3. Results of thermal fatigue test using gas flame on FGM & Conventional 8YSZ TBCs (1200°C & 1400°C)

Thermal Shock Fatigue test @1200°C			
Plasma Spray Coating at VSSC, Trivandrum			
Sl.No	Specimens	Number of cycle's	Remarks
1	Conv 8YSZ	158	Failed
2	FGM 1	155	Failed
3	FGM 2	273	Not Failed (Test Stopped)
4	FGM 3	270	Not Failed (Test Stopped)

Thermal Shock Fatigue test @1400°C			
Plasma Spray Coating at VSSC, Trivandrum			
Sl.No	Specimens	Number of cycle's	Remarks
1	Conv 8YSZ	35	Failed
2	FGM 1	35	Failed
3	FGM 2	184	Not Failed (Test Stopped)
4	FGM 3	184	Not Failed (Test Stopped)

6.4 Structural phase analysis on thermal fatigue tested specimen at 1200°C via XRD.

The XRD patterns of as-sprayed coated and thermal fatigue test specimen of conventional and various FGM configurations at 1200°C is shown in figure 7. Table 4 shows the findings.

TABLE 4. Structural phase analysis (XRD) on FGM & Conventional 8YSZ TBCs

	Reference in Fig 7	Sample Details Thermal Fatigue cycling @ 1200°C	Findings from XRD pattern	Remarks
	a	Conventional 8YSZ as-sprayed	(%) c/t-ZrO_2 =100	No destabilization
	b	Conventional 8YSZ – Failed (156 cycles)	(%) c/t-ZrO_2 =100	No destabilization
	c	FGM 1 – Failed (162 cycles)	(%) c/t-ZrO_2 = 98 (%) m -ZrO_2 = 2	Mild destabilization
	d	FGM 2- Not Failed (182 cycles)	(%) c/t-ZrO_2 = 84 (%) m ZrO_2 = 16	Significant destabilization
	e	FGM 3- Not Failed (170 cycles)	(%) c/t-ZrO_2 = 94 (%) m -ZrO_2 = 6	Moderate destabilization

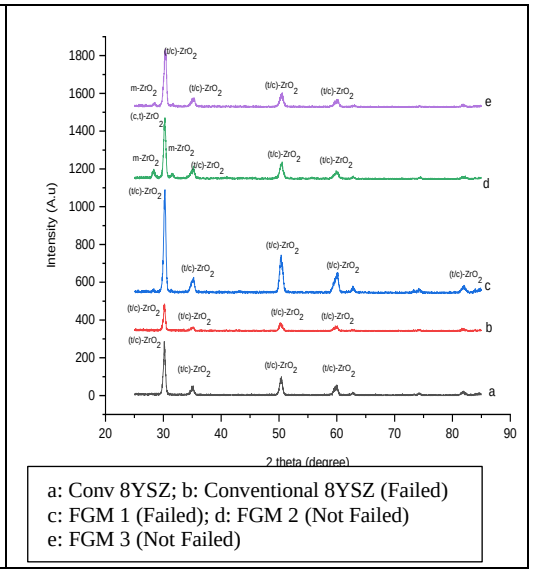


Figure 7. XRD patterns of thermal fatigue tested TBCs - conventional 8YSZ & FGM configurations at 1200^0C

Salient observations include (a) superiority of FGM 2 TBC system over Conventional 8YSZ and (b) insignificant role played by the stabilized zirconia phase in this failure and (c) thermal expansion mismatch more likely cause of failure.

6.5 Oxidation Stability test

The conventional (non-FGM) specimen failed in a span of 96 hours in oxidation stability test at 800°C, while no failure was observed among the FGM configuration even after 264 hours. Figure 8 (a,b,c) shows the TBC specimens before and after oxidation stability test at 800°C in conventional and FGM configurations.

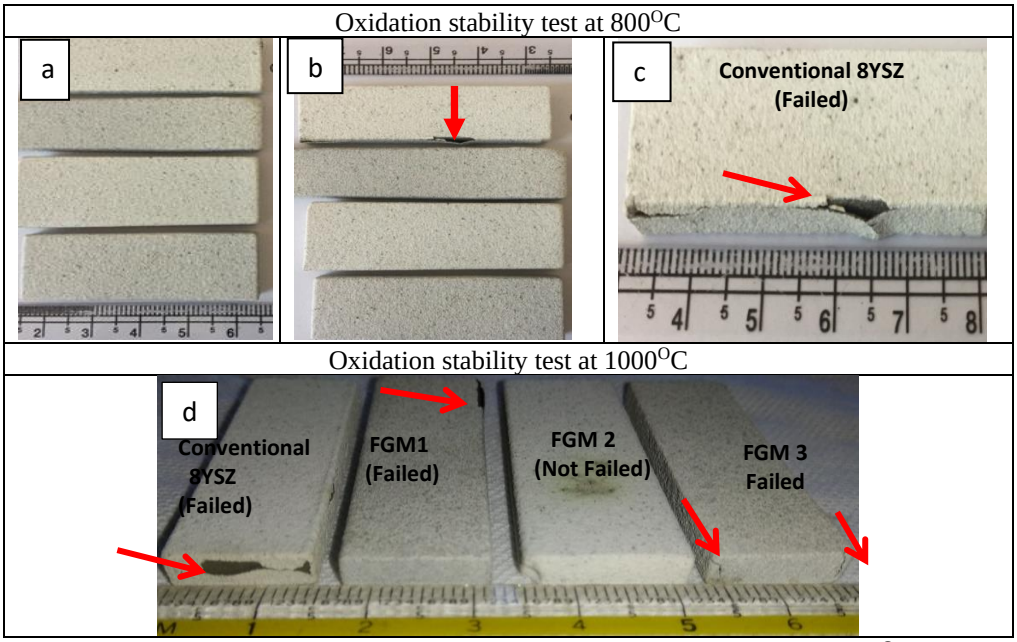
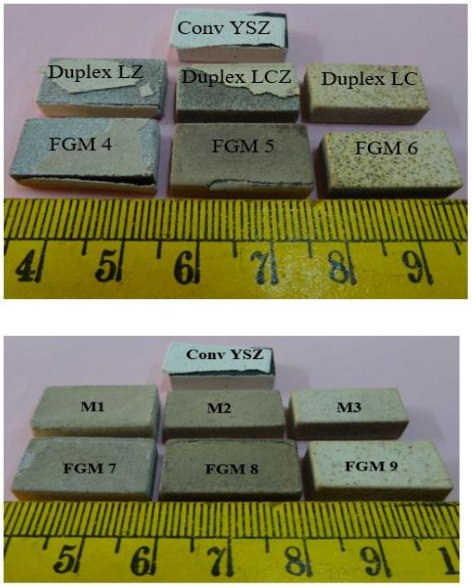


Figure 8. Specimen after oxidation stability tests (conventional 8YSZ and FGM) at 800 °C and 1000°C: (Arrows show the failure location).

In a pattern similar to that exhibited by specimen that underwent thermal shock cycle test (Flame), the conventional specimen failed in span of 24 hours at 1000℃. Only the FGM with (BC- 50BC+50TC-TC) configuration withstood an oxidation test >60 hours of oxidation stability test at 1000℃. From these experiments, while it is certain that FGM (NiCrAlY+8YSZ blend as intermediate layers between bond coat and top coat) TBCs exhibit much superior performance compared to conventional 8YSZ TBC, the exact mechanism attributable to the much superior performance of FGM TBC with FGM2 configuration alone is not clearly understood and detailed analysis is warranted to be performed. The specimen subjected to oxidation stability test at 1000^{O}C are shown in Figure 8 d.

In general, all TBCs (FGM, pyrochlore FGM and multilayer TBCs showed poor oxidation stability at 1150°C, this may be due to the long duration exposure at the high temperature and needs further investigation. It must be noted that the TBCs in this work are synthesized by using APS method which generates significant variations in coating characteristics including porosity. For best quality coatings for aerospace applications, EBPVD method alone is to be employed. However, the most valuable input derived from this research work is that (a) certain FGM configurations, and (b) integration of zirconate pyrochlores with conventional 8YSZ in multilayer format offer the best TBCs studied in this research work.

6.6 Thermal fatigue test in high temperature furnace at 1150°C on all TBCs configuration. Figure 9 shows the photographs of the various stages of TBCs thermal shock tested at 1150°C in high temperature furnace.



Specimens	Specimen Designation	Thermal fatigue@ 1150°C Cycles/Remarks)
Conventional (BC/8YSZ)	Conv 8YSZ	56 / Failed
Duplex Layer (BC/LC)	Duplex LC	124 / Not Failed
FGM (BC /wt.% (50BC-50LCZ)/ LCZ)	FGM 5	72/ Failed
FGM (BC/ wt.% (50BC-50 50LC)/ LC)	FGM 6	96/ Not Failed
FGM (BC /wt% (50BC-50 8YSZ)/ LCZ)	FGM 8	220/Failed
FGM (BC/ wt.% (50BC-50 8YSZ/ LC)	FGM 9	190/ Not Failed
Multi-Layer (BC/YSZ/LCZ)	M2	240/ Not Failed
Multi-Layer (BC/YSZ/LC)	M3	240 / Not Failed

Figure 9. Thermal fatigue test on all TBC configurations at 1150°C in high temperature furnace

Salient findings in data given in Figure 9 is the superiority of Multilayer configurations among all the TBC systems studied in this research work.

6.7 Thermal fatigue Tests using Oxy acetylene flame on all TBCs configuration.

The thermal fatigue test specimen exhibited significantly varied performance and test results between the conventional 8YSZ and all TBC configuration as shown in Table 1. The results pertain to the test when the hot face (ceramic surface) was subjected to the harsh environment (flame surface temperature at ceramic surface 1200^{o}C and 1400^{o}C). Failure was recorded when the topmost ceramic layer (visible to naked eye) either cracked or showed signs of degradation such as peeling off. Photographs obtained for TBCs subjected to same test at 1400^{o}C is not shown in this report.

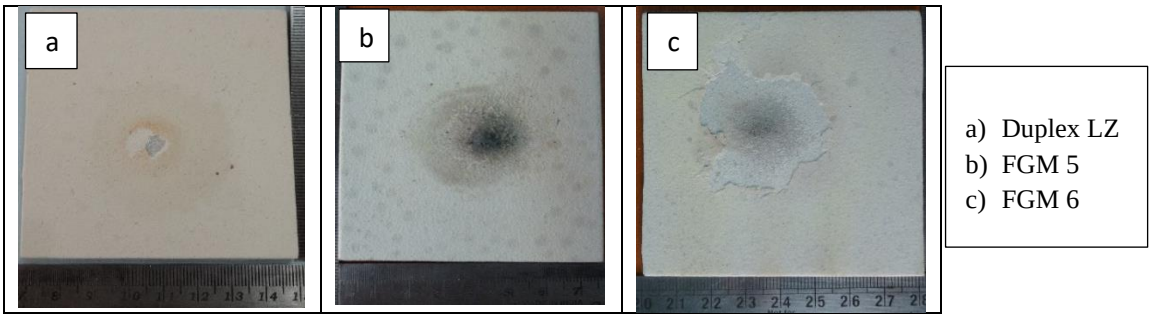


Figure 10. (a thru f): Surface of typical pyrochlore TBCs, thermal fatigue tested at 1200^{o}C

Figure 10 shows the typical ceramic topmost surface of the specimen at the end of thermal fatigue tests at 1200^{o}C. Table 5 shows the summarized results of thermal fatigue test at 1200^{o}C and 1400^{o}C.

TABLE 5. Results of Typical thermal fatigue tests using gas flame on pyrochlore (1200^{o}C and 1400^{o}C)

Specimens	Specimen Designation	Thermal Fatigue @ 1200^{o}C (Cycles/Remarks)	Thermal Fatigue @ 1400^{o}C (Cycles/Remarks)
Conventional (BC/8YSZ)	Conv 8YSZ	158 / Failed	156/ Failed
Duplex Layer (BC/LC)	Duplex LC	542/ Failed	210/ Failed
FGM (BC /wt.% (50BC-50 8YSZ)/ 8YSZ)	FGM 2	182/ Not Failed	210/ Not Failed
FGM (BC/ wt.% (50BC-50 50LC)/ LC)	FGM 6	220/ Failed	176/ Failed
FGM (BC/ wt.% (50BC-50 8YSZ/ LC)	FGM 9	546/ Failed	435/ Failed
Multi-Layer (BC/YSZ/LC)	M3	721/Failed	450/Failed

Findings from Table 5 are the following. The duplex zirconia based pyrochlore TBC's (duplex LC) exhibited superior thermal shock cycle resistance over conventional 8YSZ TBCs (Conv 8YSZ) and zirconia based FGM pyrochlores (FGM 6). Interestingly, 8YSZ and BC blend layer deposited between the bond coat and pyrochlore top coat (LC) to form FGM configuration (FGM 9) further enhanced the TBC properties and showed high potential in extending the life of coatings. Similar results were obtained for multilayer coatings as well (M3).

Typical Findings: None of the pyrochlore TBCs shown in Table 6 showed any signs of structural phase destabilization even when subjected to thermal fatigue test at 1400°C. Evidently structural

phase did not appear to have any influence on the failure of these TBCs. Most likely the failure originated from the interfaces between the coated layers. Findings from other configurations are not shown in this report.

TABLE 6. Typical Structural phase analysis results on TBCs (LZ)

SI No.	Thermal Fatigue cycling @ 1400°C	Findings from XRD pattern	Remarks
1.	Duplex LZ (as-sprayed)	(%) c/t-ZrO_2 = 100	No destabilization
2.	Duplex LZ – Failed (170 cycles)	(%) c/t-ZrO_2 = 100	No destabilization
3.	M1 – Failed (245 cycles)	(%) c/t-ZrO_2 = 100	No destabilization
4.	FGM 4- Not Failed (310 cycles)	(%) c/t-ZrO_2 = 100	No destabilization
5.	FGM 7- Not Failed (156 cycles)	(%) c/t-ZrO_2 = 100	No destabilization

6.8 Adhesion strength test results

Table 7. shows the adhesion strength results obtained from the plasma spray coatings prepared from all the compositions studied in this work.

Table 7. Typical Adhesion Strength Test Results

Sample details	Designation	Adhesion Strength, MPa (average of 2 best values out of 3)
Conventional 8YSZ	Conv 8YSZ	18.0
Duplex Layers (BC/LZ)	Duplex LZ	13.9
FGM (BC-FGM (50BC+ 50 LZ) – LZ)	FGM 4	19.4
FGM (BC-FGM (50BC+ 50 8YSZ) – LZ)	FGM7	26.41
FGM (BC-FGM (50BC+ 50 8YSZ) – LCZ)	FGM8	23.20
FGM (BC-FGM (50BC+ 50 8YSZ) – LC)	FGM9	15.79
Multilayer (BC-8YSZ-LZ)	M1	7.95

Investigation of the data obtained on adhesion strength reveals the following salient findings.

(a) Conventional 8YSZ (commercial) coatings, which has been used as reference values in the present work, exhibited a maximum adhesive strength values of 18.0 MPa (in Table 7).

(b) Around ~ 20 % improvements in adhesion strength values were observed in the coatings in FGM configurations, with blends of 8YSZ with the bond coat as intermediate layer before the pyrochlore as the top layer (FGM 4, in Table 7).

(c) Finally, in the FGM configuration involving only bond coat and respective pyrochlores (without any 8YSZ), the FGM configuration with Lanthanm zirconate (LZ) exhibited a maximum strength value of 22 MPa (FGM 7), when compared a maximum values exhibited by the other two pyrochlores (FGM 8 and FGM 9).

(d) In the multi layered configuration (BC – 8YSZ – Pyrochlore) was studied and the adhesion strength value was significant low. Other multilayer congiguration (not shown here) also possessed low adhesion strength (onr third of 8YSZ). This aspects needs further study.

7. CONCLUSIONS

1. Blends of the two plasma spray powders i.e., 8YSZ and NiCrAlY and the TBCs synthesized from these blends by using APS system exhibited superior thermal fatigue resistance over conventional TBCs of 8YSZ. Thermal fatigue tests performed on the specimen at 1200^{o}C and 1400^{o}C demonstrated the superiority of certain (50% NiCrAlY + 50% 8YSZ) blend compositions in FGM configuration. Oxidation stability tests performed on FGM TBCs confirmed the findings at 800^{o}C to 1000^{o}C. Failures in FGM configuration, especially in 50 NiCrAlY - 50 8YSZ blend composition, most likely reduced due to the gradual change in coating characteristics in FGM configuration when both, the FGM and conventional TBCs underwent tests at the same conditions.

   Thus, the superiority of FGM TBCs by using conventional 8YSZ plasma spray powder and mixed with bond coat (NiCrAlY) was established to be superior TBC configuration over the conventional 8YSZ coating.

2. Structural Phase analysis, microstructure and chemical composition confirmed the presence of pyrochlore phase zirconate in the coating. The duplex zirconia based pyrochlore and Functionally zirconia based pyrochlore TBC's exhibited superior thermal shock cycle resistance (over conventional 8YSZ TBCs).

3. 8YSZ layer deposited between the bond coat and top coat (LZ, LCZ and LC) to form multi-layered coating configuration or in FGM configuration further enhanced the TBC properties and exhibited best results among the configurations studies in this reseach study.

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PUBLICATIONS & PROCEEDINGS

I. Papers in Journals

1. **Kirti Teja Pasupuleti**, Gireesh Vishnu Prasad, Prabhu Akhil, Parvati Ramaswamy, Narayana Murty SVS, "Adhesion Strength Studies on Zirconia Based Pyrochlore and Functionally Gradient Thermal Barrier Coatings", *Materials Today: Proceedings (Elsevier)* (2019), vol. 19, pp 568-574, 2019
2. **Kirti Teja Pasupuleti**, Souvik Ghosh, Uma Manikanta Dunna, Parvati Ramaswamy, Narayana Murty SVS, "Influence of Atmospheric Plasma Spray Process Parameters on Crystal and Micro Structures of Pyrochlore Phase in Rare Earth Zirconate Thermal Barrier Coatingsm, *Materials Today: Proceedings (Elsevier),* vol.19 pp 731-736, 2019
3. **Kirti Teja Pasupuleti**, Parvati Ramaswamy, Narayana Murty SVS, "Thermal Shock and Oxidation Stability Tests to Grade Plasma Sprayed Functionally Gradient Thermal Barrier Coatings", *Front Adv Mat Res,* vol.1, pp 1-11, 2019.
4. **Kirti Teja Pasupuleti**, Souvik Ghosh, Parvati Ramaswamy, Narayana Murty SVS. "Zirconia Based Pyrochlore Thermal Barrier Coatings". Institute of Physics (IOP) Conference Series Materials Science and Engineering 577, 012099, 2019
5. **Kirti Teja Pasupuleti**, Uma Manikanta Dunna, Souvik Ghosh, Parvati Ramaswamy, Narayana Murty SVS, "Synthesis and Studies on Partially Stabilized Zirconia and Rare-Earth Zirconate Pyrochlore Structured Multilayered Coatings", Materials Today: Proceedings (Elsevier) -2019 (**Rights and Access form submitted**)
6. **Kirti Teja Pasupuleti**, Shawn Dsouza, Thejaraju R, Shankar Venkataraman, Parvati Ramaswamy, Narayana Murty SVS "Performance and Steady State Heat Transfer Analysis of Functionally Graded Thermal Barrier Coatings Systems", Materials Today: Proceedings (Elsevier), vol. 5 pp. 936-945. 2018
7. **Kirti Teja Pasupuleti**, Parvati Ramaswamy, Shankar Venkataraman, Narayana Murthy SVS, "Development of Multilayered Functionally Graded Thermal Barrier Coatings on Inconel 718 Super Alloys for Aerospace Applications", McGraw Hill Education Publication, ISBN (13): 978-93-5260-730-3: ISBN (10): 93-5260-730-9, pp. 8-13 2017.

II. Conference (Attended and presented paper)

1. International Conference on Manufacturing, Material Science and Engineering (ICMMSE 2019) organized by Department of Mechanical Engineering, CMRIT, Hyderabad August 16 – 17, 2019. (**Two Papers Presented**)
2. International Conference on Materials, Manufacturing and Modelling (ICMMM 2019) organized by the Department of Mechanical Engineering, VIT, Vellore, March 29 - 31, 2019.
3. International Conference on "Advances in Materials and Manufacturing Applications (IConAMMA 2018)" organized by the Department of Mechanical Engineering, Amrita School of Engineering, Bengaluru, August 16 - 18, 2018.
4. International Conference on Composite Materials: Manufacturing, Experimental Techniques, Modeling and Simulation (ICCMMEMS-2018) at Lovely Professional University, Jalandhar Punjab, 15-17 March 2018.
5. International Conference on Emerging Research in Civil, Aeronautical and Mechanical Engineering (ERCAM-2017), Bangalore, 21 July 2017.

   Adjudged as the ***Best paper*** in Aerospace genre.

Appendix -A

PAPERS PUBLICATIONS

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Adhesion strength studies on zirconia based pyrochlore and functionally gradient thermal barrier coatings

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ABSTRACT

Thermal Barrier Coating (TBC) plays a major role in the improvement of gas turbine and engine components in terms of their service life and performance. Generally, all coatings must possess certain primary properties to perform in the intended applications. However, regardless of applications, suitable adhesion strength is one major characteristic they must have to adequately protect the basic components on which they are applied upon. In TBCs, adhesion (or Bond) strength is a parameter that helps to illustrate the resistance of the ceramic top coat against spallation either from the bond coat (and component) or within the TBC layers itself. The performance of TBCs are reliant upon the adhesion between the coating and the metal substrate and also adhesion (or cohesion) between the bond coat and the overlying ceramic top coat layer. The de-bonding of the top coat layer or the inter-metallic bond coat layers are the main reasons of the failure of the overall TBC system. Some of the prominent problems associated with coatings applications are residual stresses, micro-cracks and pores etc. These and many other factors influence the adhesion of the coatings in addition to service environment conditions and pre coating substrate preparations such as substrate cleaning, grit blasting and very importantly plasma spray parameters. In the present work, results obtained from adhesion strength measurements carried out by following the ASTM C 633 standard test method, on various types of TBCs are being shared. Thermal barrier coatings (TBCs) were synthesized with NiCrAlY bond coat deposited on SS 304L substrate by using air plasma spray and different ceramic top coats (a) commercial 8%Yttria Stabilized Zirconia (8YSZ) (b) lab synthesized plasma spray powders of (i) Lanthanum Zirconate ($La_2Zr_2O_7$) (ii) Lanthanum Ceria Zirconate ($La_2(Zr_{0.7}Ce_{0.3})_2O_7$) and (iii) Lanthanum cerate ($La_2Ce_2O_7$). The coating depositions were carried out in different configurations i.e. two layers, three layers and gradient layers (Functionally gradient materials). The evaluation of properties includes the studies of morphology of the strength (adhesive/cohesive failure mode) tested specimen as well. General conclusions drawn from the studies on several specimen in various configurations are that cohesive failures (between the ceramic top coat layers) is the predominant mechanisms followed by few adhesive failures in bond coat coat/ceramic interface.
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1. Introduction

Since the 1950's, 8% Yttria (Y_2O_3) Stabilized Zirconia (ZrO_2), popularly known as 8YSZ has found wide application in aerospace components (gas turbines) as the standard top coat Thermal barrier Coating (TBC) material (protective over layer). This is due to its ability to withstand temperatures of up to 1200 °C without spallation in service: which involves thermal shock and possibly mechanical damage such as wear and abrasion. 8YSZ can successfully reduce the surface temperature of the substrate material to a more tolerable range which is attributable to its thermal barrier effect due to low thermal conductivity properties [1]. However, due to the continuous thermal cyclic stresses generated during service the TBC system undergoes failure. One of the key reasons for this is the coefficient of thermal expansion (CTE) mismatch at higher temperatures (1000–1200 °C) [2]. In order to overcome this problem the concept of Functionally Graded Materials (FGM) has

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been introduced [3]. FGM materials are a mixture of the bond coat (BC) and top coat (TC) in varying ratios [4]. This FGM layer is placed in between the bond coat (NiCrAlY) and top coat (8YSZ) playing the role of an intermediate layer that minimizes the CTE mismatch at elevated temperatures. Generally Atmospheric Plasma Spray (APS) coating is a popular method to apply the coatings.

To increase the in-service performance temperature of this metal, thermally insulating materials (in the form of coatings) having very low thermal conductivity are required [5]. Currently, the most commonly used TBC material is 8YSZ which not only possesses low thermal conductivity (~2.2 W/mK) but performs well (withstands thermo-mechanical stresses) efficiently [6]. In order to attain increased efficiency and durability, the present day need is to increase the service temperatures >1200 °C by newer materials and configurations. This technological requirement warrants development of newer TBC materials with thermal conductivities lower than 8YSZ but without compromising on other materials characteristics such as thermal shock resistance, adhesion, microstructure etc [7]. Zirconia based materials/coatings with pyrochlore structures (a derivative of fluorite) have shown high potential as a TBC to serve at ~1400 °C, due to their favourable thermal insulating characteristics [8,9]. In addition to thermal and structural characteristics, adhesion strength of the TBC with the substrate/component also is an important property to be studied to find a suitable replacement to 8YSZ. Therefore, many configurations involving suitable combinations of different ceramic layers (8YSZ and pyrochlore composites) are also being widely researched [10].

1.1. Adhesion strength test

Adhesive bonding may involve different mechanisms that occur simultaneously during the coating process, with varying intensities. The most important one in the process of APS is the joint formed due to substrate surface roughness [11,12]. The adhesion of the coating is dependent on surface cleaning of the substrate, grit blasting methodologies, coating parameters and surrounding [13]. A generally accepted adhesion strength test in the case of APS coatings is the tensile adhesion strength test according to the ASTM-C633 standard [14,15]. The specimen preparation involves coating the pull rods and to test the load at which both the parts in the pull rods get separated under tensile loading. The test mechanism briefly is: the delamination or separation of the pull rods during tensile test may be at the (a) substrate-bond coat-top coat interface or (b) within the top coat layers themselves.

2. Scope of the present work

Commercial NiCrAlY (AMDRY 962) bond coat (BC), 6–8% Yttria stabilized zirconia (8YSZ) (METCO 204NS) and lab synthesized ceramic top coat pyrochlore plasma spray powders of (i) Lanthanum Zirconate ($La_2Zr_2O_7$): abbreviated as LZ (ii) Lanthanum Cerium Zirconate (La_2 $(Zr_{0.7}Ce_{0.3})_2O_7$: abbreviated as LCZ and (iii) Lanthanum Cerate ($La_2Ce_2O_7$): abbreviated as LC, were used as the starting materials. The ceramic top coats (TC) were plasma sprayed on the bond coat and functionally gradient layer (FGM) of wt% (50BC-50TC). The coating depositions were carried out on stainless steel (SS 304L) pull rods (dimensions and thickness as per the ASTM C-633 standard) by using air plasma spray (APS) method. The coated and grit blasted surface were glued by using suitable adhesive and the tensile test was carried out by using Universal testing Machine (UTM). Evaluation of other properties included studies of adhesion strength tested surface morphology, microstructure and determination if the failure pertained to adhesive and/or cohesive mechanism.

2.1. Experimental procedure

Lab synthesized LZ, LCZ and LC spray powder compositions were prepared via solid state mixing, calcination and manual plasma spray powder synthesis method. The bond coats (AMDRY 962-Sulzer METCO) and ceramic top coats were deposited by APS method. Spray Parameters for metallic and ceramic materials are presented in Table 1. The plasma spray powders were spray coated on SS (304L) substrate of dimensions (∅ 25.4 mm × 150 mm) for the tensile adhesion strength tests. The surface to be coated were degreased using acetone and grit blasted at 45° incidence angle with a blasting distance of 100 mm. The samples were placed in a fixture sample holder and sprayed on substrate surface. SEM and XRD was employed to reveal phase content of the lab synthesised plasma spray powder and deposits. Adhesion of the coating systems was measured using ASTM-C633 standard method.

The adhesive used in the adhesion strength test was the HTK Ultra bond cured for 50 min at 180 °C and the contact pressure used for bonding should not fall below 20 N/cm^2. The configurations of the specimen of TBC's system designations used in this work are shown in Table 2.

The coating and substrate-coating interface morphology after the adhesion strength test was inspected on each tested specimen by using a low power (10X) microscope. Scanning Electron Microscope (SEM) associated with Energy Dispersive X-Ray spectroscopy (EDS) was employed to study the spray powder morphologies and spray coatings microstructure (prepared on 25 mm × 10 mm × 5 mm (thickness) coupons, simultaneously along with the pull rods during coatings process).

Fig. 1 Various stages involved in the adhesion strength test procedure left to right (a) pull rod surfaces before and after grit blasting (b) ceramic coated surfaces (c) specimen ready for application of adhesive (d) mounting of the glued specimen in the fixture (e) fixture placed inside the high temperature oven (f) specimen after delamination after adhesion strength testing (arrow in figure shows pull rods separation).

Table 1
Plasma Spray Coating Parameters.

Plasma Spray Parameters (P)	NiCrAlY (Bond Coat)	8YSZ (Top Coat)	LZ/LCZ/LC (Top Coat)
Voltage (V)	75	70	60
Current (A)	400	550	400
Power (kW)	24	35	24
Primary gas, Ar (SLPM)	57	38	14
Secondary gas, H_2 (SLPM)	17	19	5
Power feed rate (g/min)	45	35	10
Spray distance (mm)	100	100	100

Table 2
Specimen Designation.

Sl .No	TBC's System	Specimen Designation
1.	Conventional (BC/8YSZ)	C
2.	Duplex Layers (BC/LZ)	D1
3.	Duplex Layers (BC/LCZ)	D2
4.	Duplex Layer (BC/LC)	D3
5.	Multi-Layer (BC/YSZ/LZ)	M1
6.	Multi-Layer (BC/YSZ/LCZ)	M2
7.	Multi-Layer (BC/YSZ/LC)	M3
8.	FGM (BC/wt% (50BC-508YSZ)/LZ)	FGM1
9.	FGM (BC/wt% (50BC-508YSZ)/LCZ)	FGM2
10.	FGM (BC/wt% (50BC-508YSZ)/LC)	FGM3
11.	FGM (BC/wt% (50BC-50LZ)/LZ)	FGM4
12.	FGM (BC/wt% (50BC-50LCZ)/LCZ)	FGM5
13.	FGM (BC/wt% (50BC-50LC)/LC)	FGM6

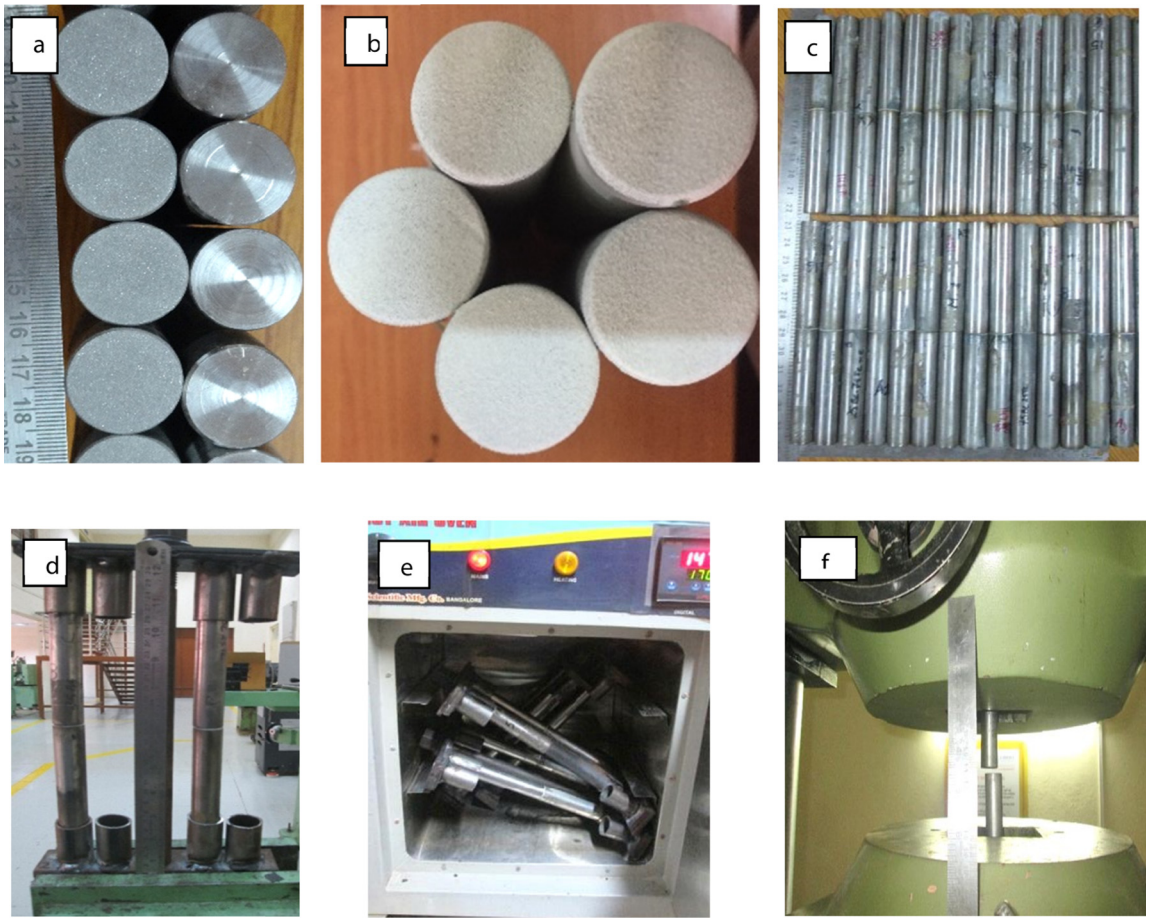

Fig. 1. Various stages involved in the adhesion strength test procedure left to right (a) pull rod surfaces before and after grit blasting (b) ceramic coated surfaces (c) specimen ready for application of adhesive (d) mounting of the glued specimen in the fixture (e) fixture inside high temperature oven and (f) specimen after delamination after adhesion strength testing. (arrow in figure shows pull rods separation).

3. Results

3.1. Chemical compositional analysis

As already informed in the previous sections, three pyrochlore powder compositions were synthesized and were converted into flowing plasma sprayable powders in the laboratory. Details of the plasma sprayable powders synthesis is published elsewhere [16]. Chemical compositional analysis of as-sprayed coatings prepared from these lab synthesized plasma sprayable pyrochlore powders were carried out by performing EDS analysis associated with SEM.

Fig. 2 shows the micrographs, EDS patterns and chemical composition of the three types of pyrochlore studied in this work which are detailed as the following (a) LZ (b) LCZ and (c) LC.

3.2. Microstructural analysis of pyrochlore plasma spray coated surfaces

SEM micrographs obtained from plasma spray coated pyrochlore surfaces were similar in all the three materials i.e. LZ, LCZ and LC. Typical micrograph is shown in Fig. 3 – at (a) 3000× and (b) 5000× magnifications. Spherical molten grains of dimensions varying between sub-micron and up to nearly 80 μm were the salient features. Fine micro cracks in isolated areas over the grains were also observed, that likely were not significant.

3.3. Crystallographic structural phase analysis of As-sprayed coating

XRD patterns obtained from plasma spray coated pyrochlore surfaces were analysed to study the crystal structural phases present and to assess if the reactions were complete after the process of plasma spray coating in all the three materials i.e. LZ, LCZ and LC. Fig. 4 shows the XRD pattern obtained from Lanthanum Zirconate Pyrochlore plasma spray coated surface, which as expected, depicted a single phase formation of $La_2Zr_2O_7$. No unreacted zirconia or lanthanum oxide peaks were found to be present in the pattern.

XRD patterns obtained from plasma spray coated surfaces of LCZ and LC pyrochlore exhibited the desired patterns which were single phased, and comprised of $(La_2\ (Zr_{0.7}Ce_{0.3})_2O_7)$ and $La_2Ce_2O_7$ respectively. XRD patterns for these two pyrochlore are not shown.

3.4. Adhesion strength test results

Table 3 shows the adhesion strength results obtained from the plasma spray coatings prepared from all the compositions studied in this work.

The surfaces of the pull rods, after the completion of the adhesion strength tests are shown in Fig. 5.The adhesive is of high strength and in all cases the mode of failure was either due to the failure of one of the bond coat-top coat interface or top coat layers.

In addition to the load at which the pull rods detached, i.e. coatings failed, Table 3 also shows the most likely modes of failure, i.e

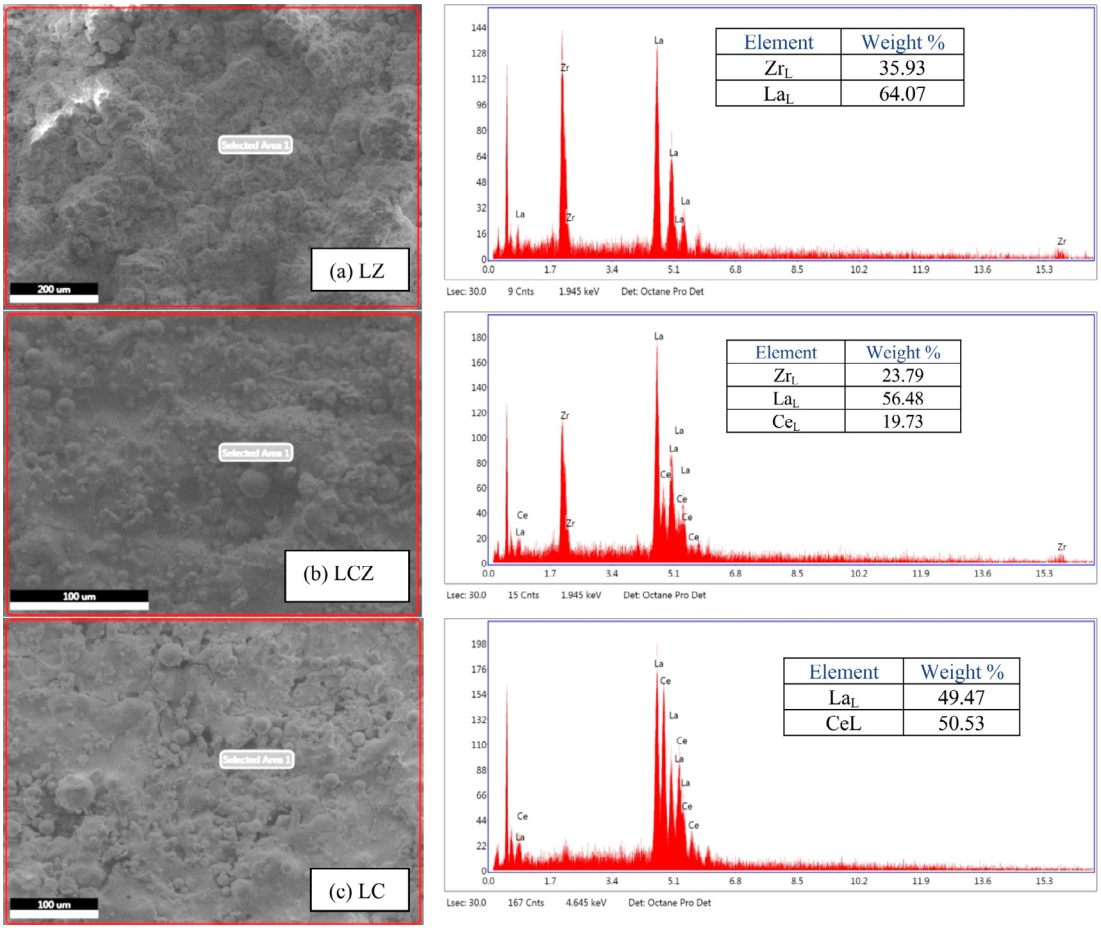

Fig. 2. Micrograph, EDS pattern and chemical composition of pyrochlore as – spray coated surfaces. The chemical compositions of the three pyrochlore (a) LZ (b) LCZ and (c) LC were found to be as per the desired and synthesized composition.

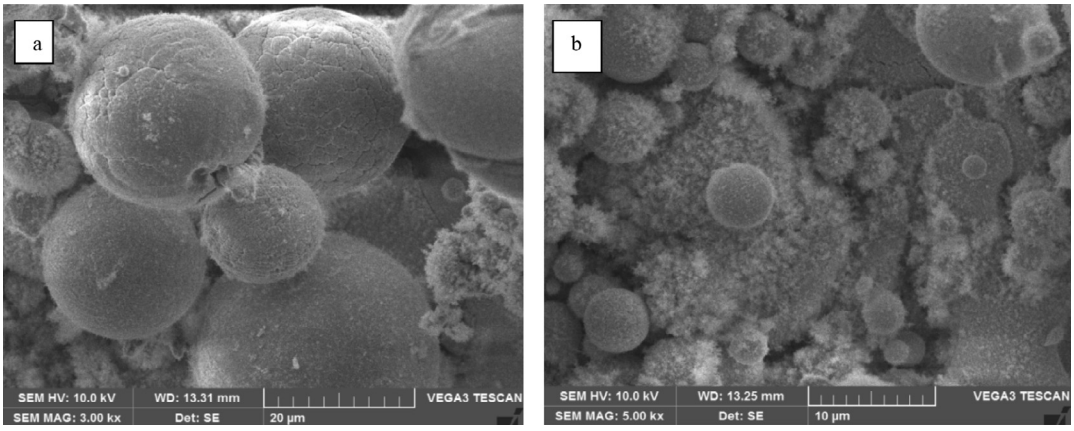

Fig. 3. SEM Micrograph of LZ plasma as-sprayed coated surface: a) 3000× b) 5000×.

adhesive or cohesive, or mixed mode. Preliminary investigation of the data obtained reveals the following salient findings.

(a) Conventional 8YSZ (commercial) coatings, which has been used as reference values in the present work, exhibited a maximum adhesive strength values of 18.0 MPa (serial number 1 in Table 3). When absolute values are considered, this appears to be only half of the adhesion strength obtained for commercial plasma sprayed 8YSZ TBCs (~36.0 MPa) [17]. At this stage it must be pointed out that, in addition to powder quality, plasma spray coating qualities are highly dependent upon the spray coating parameters and pre coating specimen preparation. Further the adhesion strength measurement practices also highly influence the characteristics. Considering that (a) all the spray coated specimen were prepared by using the same APS equipment under identical conditions of specimen pretreatment, and (b) adhesion strength tested under identical condition: rather than focussing on the absolute adhesion strength values, the relative values

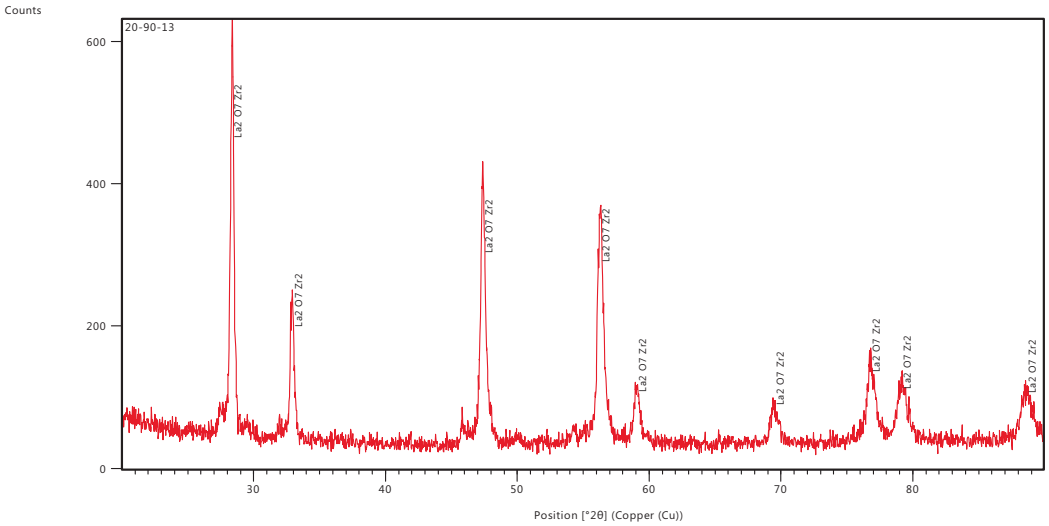

Fig. 4. XRD pattern of LZ plasma as-sprayed coated surface.

Table 3
Adhesion Strength Test Results.

Serial Number	Sample details	Desig-nation	Specimen	Ultimate Tensile Load		Failure Mode Cohesive/Adhesive	Adhesion Strength, MPa (average of 2 best values)
				kN	MPa		
1	Conventional YSZ	C	i.	9.2	18.1	Cohesive	16.75
			ii.	4.8	9.4	Cohesive	
			iii.	7.8	15.4	Cohesive	
2	Duplex LZ	D1	i.	4.4	8.6	Cohesive	13.90
			ii.	6.4	12.6	Cohesive	
			iii.	7.7	15.2	Cohesive	
3	Duplex LCZ	D2	i.	2.8	5.5	Mixed mode	7.25
			ii.	3.3	6.5	Mixed mode	
			iii.	4.1	8.0	Mixed mode	
4	Duplex LC	D3	i.	2.3	4.5	Mixed mode	6.80
			ii.	3.1	6.1	Mixed mode	
			iii.	3.8	7.5	Mixed mode	
5	Multilayer BC-8YSZ-LZ	M1	i.	4.4	8.6	Mixed mode	7.95
			ii.	3.7	7.3	Mixed mode	
			iii.	2.1	4.1	Mixed mode	
6	Multilayer BC-8YSZ-LCZ	M2	i.	3.7	7.3	Cohesive	6.40
			ii.	2.8	5.5	Cohesive	
			iii.	1.4	2.7	Cohesive	
7	Multilayer BC-8YSZ-LC	M3	i.	2.1	4.1	Cohesive	5.50
			ii.	2.5	4.9	Cohesive	
			iii.	3.1	6.1	Cohesive	
8	FGM BC-FGM(50BC + 50 8YSZ)-LZ	FGM1	i.	12.6	24.8	Adhesive	26.41
			ii.	14.2	28.02	Adhesive	
			iii.	3.8	7.5	Adhesive	
9	FGM BC-FGM(50BC + 50 8YSZ)-LCZ	FGM2	i.	12.1	23.90	Mixed mode	23.20
			ii.	11.4	22.51	Mixed mode	
			iii.	10.2	20.1	Mixed mode	
10	FGM BC-FGM(50BC + 50 8YSZ)-LC	FGM3	i.	7.4	14.6	Cohesive	15.79
			ii.	8.6	16.98	Cohesive	
			iii.	5.8	11.45	Cohesive	
11	FGM BC-FGM(50BC + 50 LZ) -LZ	FGM4	i.	11.4	22.51	Adhesive	19.94
			ii.	7.2	14.20	Adhesive	
			iii.	8.8	17.38	Adhesive	
12	FGM BC-FGM(50BC + 50 LCZ)-LCZ	FGM5	i.	7.5	14.81	Adhesive	12.50
			ii.	4.4	8.6	Adhesive	
			iii.	5.2	10.2	Adhesive	
13	FGM BC-FGM (50BC + 50 LC)-LC	FGM6	i.	2.4	4.7	Mixed mode	7.95
			ii.	3.8	7.5	Mixed mode	
			iii.	4.3	8.4	Mixed mode	

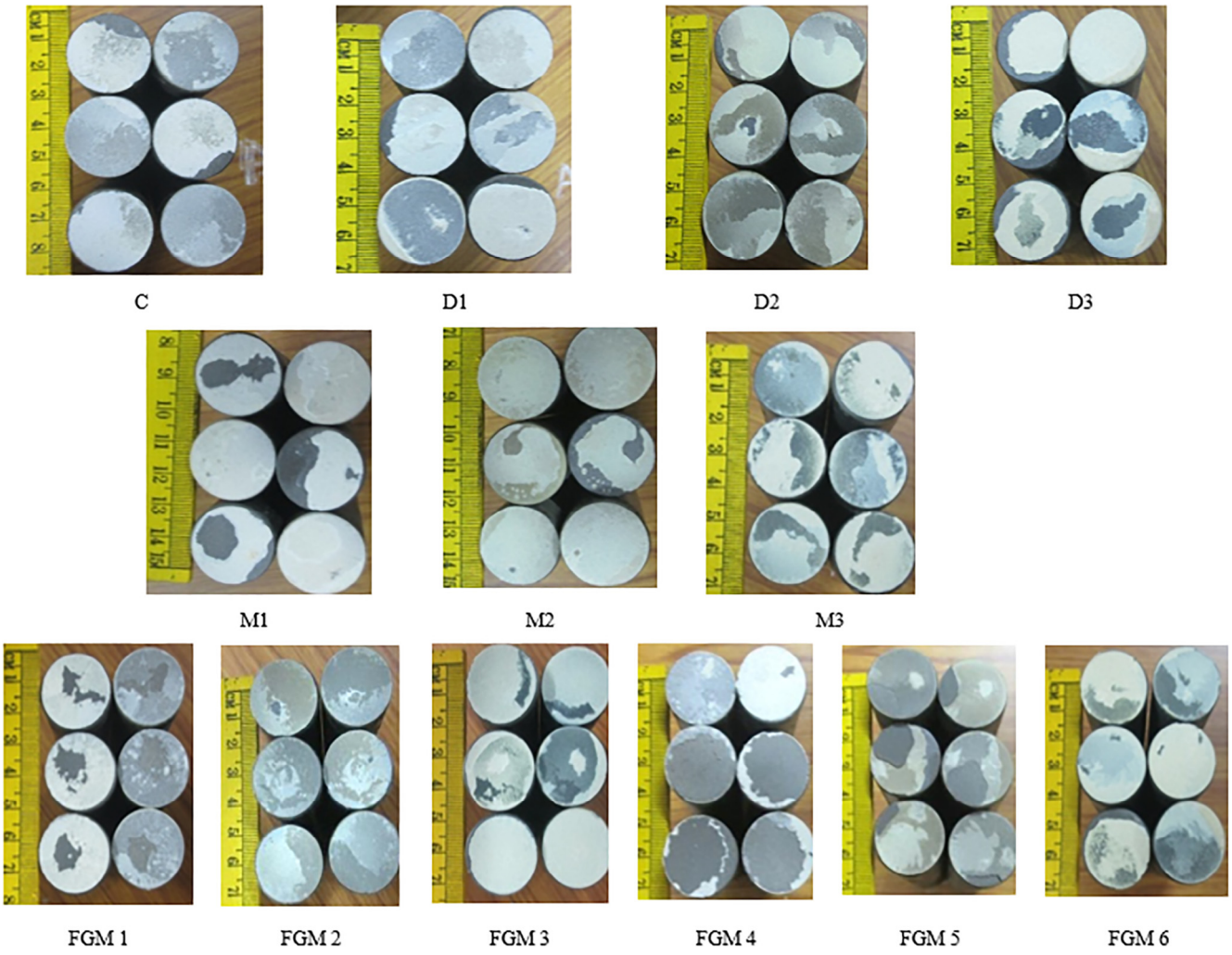

Fig. 5. Surfaces of the pull rods, after the completion of the adhesion strength tests.

of strength obtained are being considered here with an aim to grade the various coatings studied in this work.

(b) Duplex layer Lanthanum Zirconate (bond coat and LZ top coat) appears to exhibit higher adhesion strength (double) when compared to Duplex layer Lanthanum Cerium zirconate (LCZ) and Lantahnum Cerate (LC) among the pyrochlores studied in duplex (only two layers: i.e. bond coat and top coat) mode (serial number 2 viz 3 and 4 in Table 3).

(c) In the multi layered configuration (BC – 8YSZ – Pyrochlore), none of the strength values were encouraging (serial numbers 5, 6 and 7 in Table 3).

(d) Remarkable improvements in adhesion strength values were observed in the coatings in FGM configurations, with blends of 8YSZ with the bond coat as intermediate layer before the pyrochlore as the top layer (serial numbers 8, 9 and 10 in Table 3). Here again the best result (maximum of 28.0 MPa) was obtained for the top coat layer of LZ (serial number 8 in Table 3).

(e) Finally, in the FGM configuration involving only bond coat and respective pyrochlores (without any 8YSZ), the FGM configuration with Lanthanm zirconate (LZ) exhibited a maximum strength value of 22 MPa (FGM 4), when compared a maximum values exhibited by the other two pyrochlores (FGM 5 and FGM 6).

4. Conclusions

Adhesion strength determination of coatings synthesized from commercial 8YSZ, lab synthesized pyrochlores (zirconates with Lanthanum and Cerium oxides) in duplex and functionally graded configurations (FGM) revealed a general pattern of favourable characeristics by some coating materials and configuration. Lanthanum zirconate ($La_2Zr_2O_7$) coatings in duplex layers and in functional graded configurations as well, exhibit favourable adhesion strength values in spray-coated conditions. Adhesion strength is one of the basic qualities a TBC must possess and the results obtained in this exercise point towards the development of a high quality coating by considering lanthanum zirconate in functionally graded coating configuration. This is because pyrochlore coatings are also likely to be suitable for other improved characteristics to serve as TBCs due to their superior thermal stability at temperatures > 1200 °C.

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Influence of atmospheric plasma spray process parameters on crystal and micro structures of pyrochlore phase in rare earth zirconate thermal barrier coatings

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ABSTRACT

Yttria-stabilized zirconia (YSZ) thermal barrier coatings is most widely used in gas turbine engines applications and its primary role is to protect the underlying base metal from degradation at its high temperature (>1000 °C) service environment. While YSZ serves well in this role, materials with higher thermal stability and lower thermal conductivities are required to be developed for attaining higher operating temperatures and thereby higher energy conversion efficiencies. A number of rare-earth zirconates which form the cubic fluorite-derived pyrochlore structures ($A_2B_2O_7$) where A: La, Gd, Sm, Ce and B: Zr are being developed, some compositions are more attractive due to their good amalgamation of thermal and mechanical properties. However, when these materials are plasma spray coated on metal substrates, the favorable properties are not immediately realized due to various contributing factors such as poor adhesion/cohesion, microstructure (porosity, defects) or even incomplete stabilization or destabilization of the desired phase (crystal structure) after passing through the plasma. In this paper, plasma sprayable powders of zirconate pyrochlores (or with disordered fluorite structures) synthesized from using La and Ce as the trivalent "A" cation, were plasma sprayed onto Inconel 718 substrates, by using different plasma spray parameters. The considerable influence of these spray parameters on the structural phases (analyzed via XRD) and microstructures (studied via SEM on polished cross section metallographs) are presented in detail.
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1. Introduction

Gas turbine engines perform at high service temperatures which may be taken even upto 1200 °C with the desire to improve their energy efficiency and power output. Gas turbines must be facilitated to function at as high temperature as may be practically possible to maximize their efficiency, without compromising on safety aspects [1]. Until about a couple of decades ago, the thrust to achieve this was by improving the alloy design, modified microstructures, superior most single crystal development and also by providing internal cooling to the turbine blades by air flow through internal channels cast into the component [2]. To achieve higher performance, the service temperatures must be increased and currently this is realized via application of Thermal Barrier Coatings (TBCs) with a goal to protect the superalloys from degradation at the operating temperatures. 8%Y_2O_3-stabilized ZrO_2 (8YSZ) TBCs, applied either by Electron Beam Physical Vapor Deposition (EBPVD) or Atmospheric Plasma Spray Coating (APS) has been the state of the art coating material since the eighties and these TBCs have been enabled by deposition on high-temperature gas turbine components for improved performances [3].

TBCs are complex, multifunctional thick films (typically 100 μm–2 mm thick) of a refractory material that protect the metal part from the extreme temperatures in the machine. Undeniably, in the hottest part of many gas turbine engines, the coatings enable metallic materials to be used at gas temperatures above

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their melting points [4]. Under such heat flux conditions, it is the thermal conductivity of the coating that dictates the temperature drop across the TBC: however, the other major contributors towards the use of any TBC in the application are (a) adhesion characteristics (b) microstructure (grain morphologies, porosity, defects etc) (c) Thermal expansion characteristics and also (d) mechanical and phase (crystal structure) stability. Therefore, it is important to be aware that not all materials with low thermal conductivities alone may serve as good TBC candidates. While 8YSZ in its metastable tetragonal-prime structure is the current material of choice for TBCs because of its proven ability as a highly durable TBC material, next generation turbines are expected to be capable of operating at higher temperatures and for longer times than 8YSZ. Therefore, the search is underway for TBCs that will replace 8YSZ and if not, they will at least compliment 8YPSZ in a befitting manner, say by forming composite layers with 8YPSZ.

Y_2O_3 as a suitable stabilizer to ZrO_2 was attributed to its capability to serve under severe thermal cycling conditions. The low and temperature-independent thermal conductivity of YSZ was attributed to the presence of a high point defect concentration associated with the substitution of Zr^{4+} ions by Y^{3+} ions in the fluorite structure, producing a small spacing between point defects. As an oxygen vacancy is introduced into the zirconia structure for every two Y^{3+} ions that substitute for a Zr^{4+} ion, the average distance between oxygen vacancies is favorably affected [5]. The new insight that a large concentration of defects changes the vibrational modes from pure phonons in un-doped, monoclinic zirconia to a variety of other modes in 4 mol% YSZ, even though the material remains crystalline, may prove to be important in identifying new candidate TBC materials [5].

Thus, in recent times, the research efforts are being directed towards the development of materials that may serve as TBCs in new generation gas turbines. While other fluorites did not offer any outstanding materials, attention was diverted towards Pyrochlores: $A_2^{3+}B_2^{4+}O_7$, especially zirconate pyrochlores. Pyrochlores, being disordered fluorite structures are also related with the fluorite structures, have lower thermal conductivity than YSZ. This class of materials is also of fundamental interest because of the close relationship between the fluorite and pyrochlore structures. The pyrochlore $Y_2Zr_2O_7$ is actually unstable to the disordered fluorite material $(ZrO_2)_2$-Y_2O_3, i.e. heavily doped YSZ. However, replacing the Y^{3+}ion with larger ions, such as La^{3+} or Gd^{3+}, results in a stable pyrochlore structure up to at least 1500 °C.

In the quest for finding newer compositions, in the class of zirconates based pyrochlores, Rare Earths (RE) such as La, Gd, Sm, Nd etc. have been found to suit the requirements of the "A"$^{3+}$ions and the "B" sites are naturally occupied by Zr^{4+} [6]. Co-doping of pyrochlores on both A and B sites has also been proposed to further reduce their conductivity and also to modify their thermal expansion coefficients [7]. Regardless of the materials composition and the stringent methods adopted in their synthesis to arrive at the perfect blend of composition with the most desired structural phase, it is important to note that the APS process involves a number of spray parameters to be set in the spray machine and these parameters strongly dictate the coating quality. This paper describes the influence of plasma spray meters on the phase stabilization of pyrochlore structure in RE Zirconate TBCS as well as the microstructural developments.

2. Experimental work

In the present work, plasma sprayable powders synthesized in the laboratory by ball milling and subjected to thermal treatments from the following three different compositions (a) Lanthanum zirconate, (b) Lanthanum cerate and (c) Lanthanum cerium zirconate were used as the starting materials. Details of powders synthesis have been reported elsewhere [8]. Initially ~50 to 75 μm thick NiCrAlY bond coat (AMDRY 962) were plasma spray coated on grit blasted (for roughening the surface for mechanical bonding) and de-greased (with solvent) Inconel 718 substrates (25 mm × 10 mm × 5 mm (Thickness)). The ceramic coatings (pyrochlore top coats) were plasma spray coated (intended thickness ~400 to 500 μm) on the bond coated surfaces. Other than the spray parameters all other processing conditions such as preheating of spray powders, substrate preparation, number of passes etc., were maintained the same.

Table 1 gives the composition details and designations used in this research paper. The three compositions were plasma spray coated by using three different spray parameters each. Thus nine different types of coatings were obtained. Table 2 gives the details of the spray conditions and configurations used.

2.1. Thermal and materials analysis

The coated specimen was subjected to the following thermal and materials analysis.

a. Structural phase analysis of the as-sprayed coated surface via X-ray Diffractometry (XRD)
b. Microstructural analysis on polished cross section metallographic specimen removed from spray coated samples via Scanning Electron Microscopy (SEM)
c. Determination of the life of coated specimen when thermal shock cycled between 1150 °C and ambient (forced air cooling) at room temperature, to determine the best parameter of plasma spray coating. Details of the test are published elsewhere [9].

The main objective of this research work was to make a preliminary assessment if the plasma spray parameters had any major influence on the performance of the coatings and this was carried out by evaluating which composition and plasma sprayed under which parameter could withstand the maximum number of thermal shock cycles between 1150 °C and ambient under forced air cooling. The assessment included analysis of the XRD patterns of the coatings sprayed under different parameters (P1, P2 and P3) and matching the thermal shock cycle test results.

3. Results

Fig. 1 shows the photographs of the various stages of specimen prepared and thermal shock tested. Table 3 shows the number of thermal shock cycles withstood by each specimen (described in Tables 1 and 2).

3.1. Salient findings on microstructures

Fig. 2 shows the SEM micrographs of the polished cross section metallographs removed from the as-sprayed coatings, synthesized under the different parameters shown in Table 2.

Table 1
Compositions and designations.

Compositions	Chemical formula	Designation	Coating configuration
Lanthanum zirconate	$La_2Zr_2O_7$	LZ	BC-TC
Lanthanum Cerium Zirconate	$La_2(Zr_{0.7}Ce_{0.3})_2O_7$	LCZ	BC-LCZ
Lanthanum Cerate	$La_2Ce_2O_7$	LC	BC-LC

Table 2
Plasma spray coating parameters.

Plasma Spray Parameters	NiCrAlY (Bond Coat)	P1 (Top coat)*	P2 (Top coat)*	P3 (Top coat)*
Voltage (V)	60	60	60	60
Current (A)	400	350	450	400
Power (kW)	24	21	27	24
Primary gas, Ar (SLPM)	57	37	35	14
Secondary gas, H_2 (SLPM)	17	8	4	5
Spray distance (mm)	100	100	100	100

* For all compositions and spray configurations – LZ or LCZ or LC.

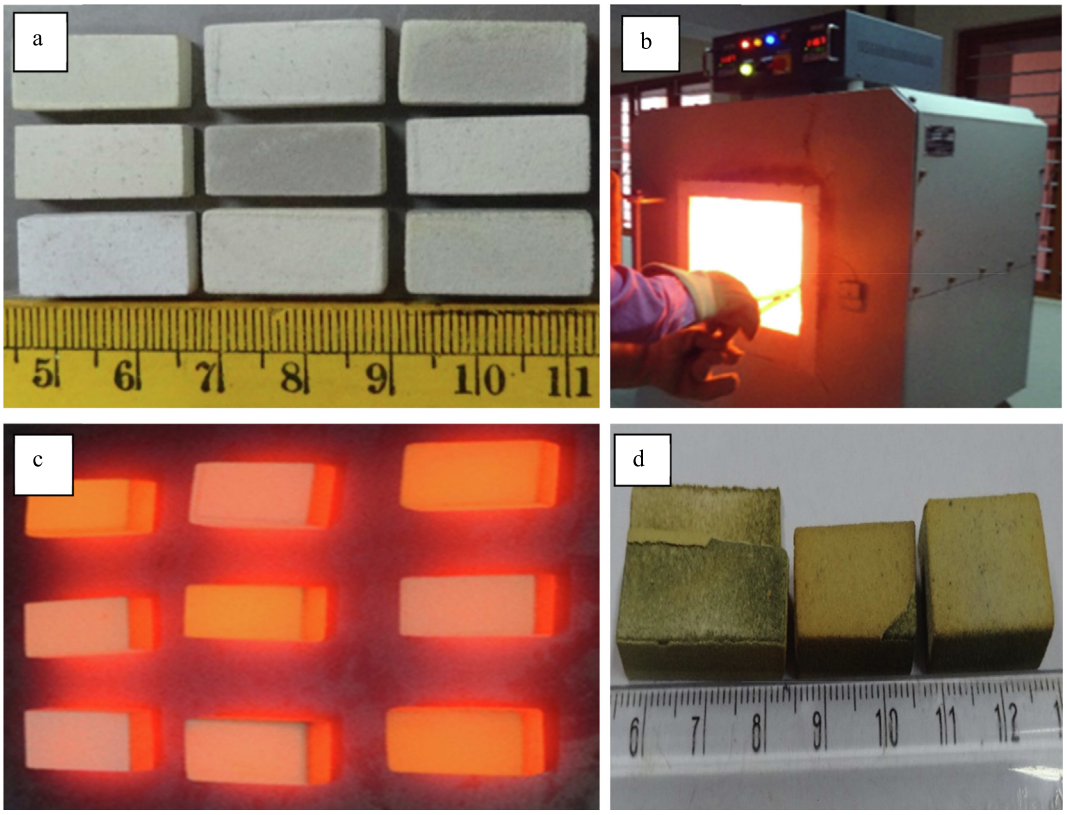


Fig. 1. They have been depicted as (a) as-spray coated specimen, (b) thermal shock cycling test (introduction into furnace at 1150 °C), (c) specimen removed from furnace after completion of one thermal shock cycle and (d) specimen of one composition (typical) after completing thermal shock cycle tests (two specimen have failed and one is intact).

Table 3
Number of thermal shock cycles to failure (1150 °C and ambient at room temperature).

Parameters	LZ/Number of Cycles	LCZ/Number of Cycles	LC/Number of Cycles
P1	15/F	15/F	30/F
P2	07/F	15/F	40/F
P3	30/F	20/NF	48/NF

Note: F – Failed; NF – Not Failed.

Micro structural analysis of the as sprayed polished cross section metallographic specimen, when studied under SEM, revealed the substrate, bond coat and the top coat layers. Distinguishing features were that all the specimen when plasma sprayed by using parameter P3 exhibited a fairly smooth, defect free, good thickness build up and sound interface. In contrast, the interfaces of the as sprayed coatings when synthesized under parameters P1 and P2 were uneven, jagged and rough with significant amounts of porosities and grain pull outs. This pattern was found to be the same for all the three compositions, i.e. LZ, LC and LCZ.

Fig. 3 shows the XRD patterns and data corresponding to coating sprayed by using each spray parameter. The standard data for each material composition, i.e. Lanthanum Zirconate, Lanthanum Cerium Zirconate and Lanthanum Cerate are also provided along with in the same figure.

4. Discussion

a) All the specimen thermal shock cycled within the experimental framework of this research paper exhibited superior or somewhat better thermal shock resistance when synthesized under parameter P3. This finding is based on the results shown in Table 3 where, without exception specimen labeled as LC, LZ and LCZ when processed under plasma spray parameter P3 withstood more number of shock cycles. In some cases the experiments were not taken to failure because the objective of this work was to determine if any one of the potentially good spray parameters emerged superior to the other two. This objective was met with and P3

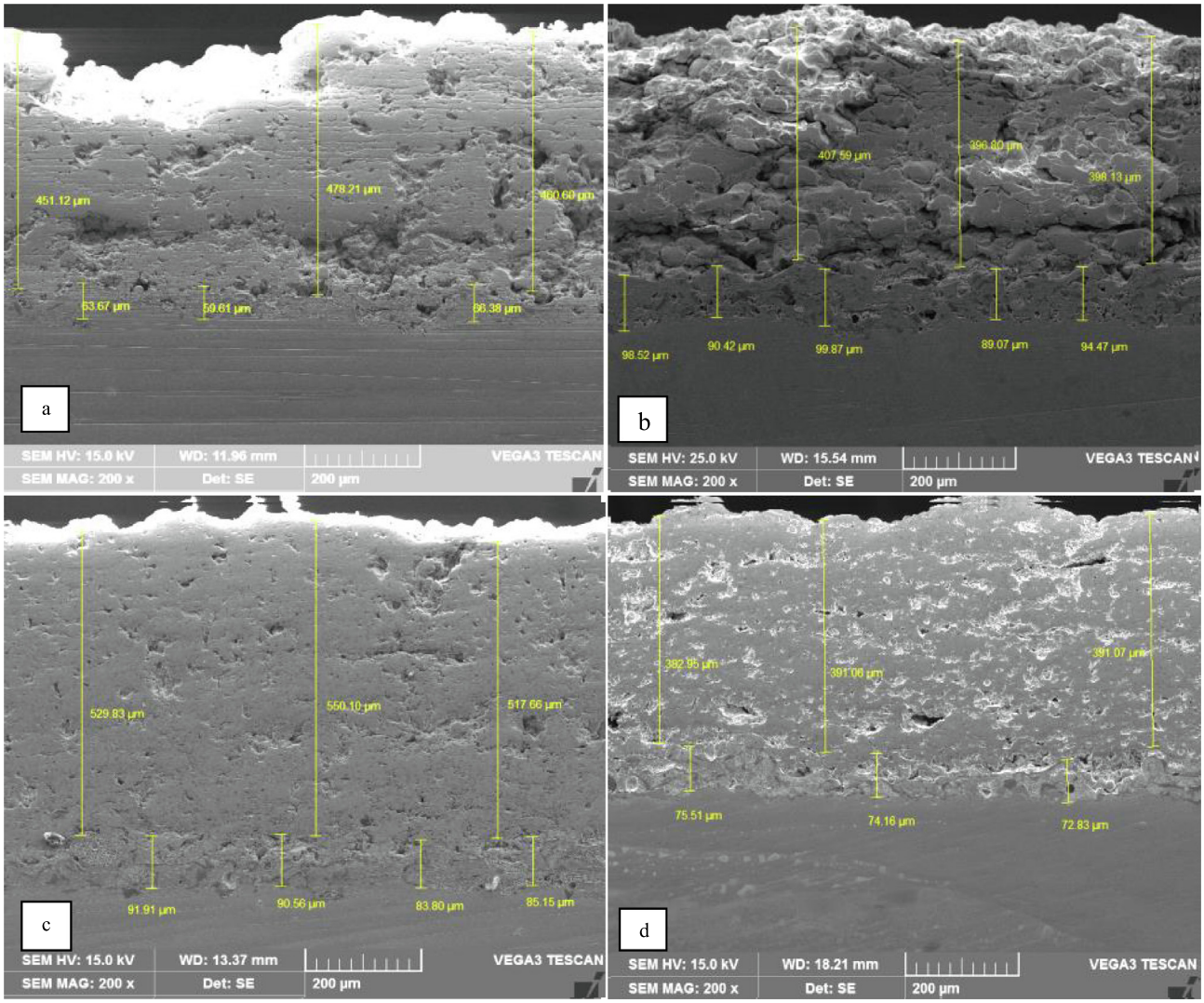


Fig. 2. SEM Micrographs on Polished Cross section metallographs removed from typical as spray coated specimen under the three spray process parameters (P1, P2, P3): (a) P1-LCZ; (b) P2-LZ; (c) P3-LC; (d) P3-LZ.

was confirmed to be the most suitable parameter for these compositions to be spray coated for all the work under this research program.

b) Microstructural analysis revealed good interface characteristics in coating sprayed with P3 parameters.

c) XRD patterns from as sprayed specimen processed under all the three spray parameters, shown in Fig. 3 were analyzed and the salient findings are the following

   i) All the nine as-spray coatings (3 compositions and 3 plasma spray parameters) closely matched with the standard data of the three compositions when the inter-planar spacings (d-spacings) were considered.

   ii) While no shift in the d-spacings were apparent, major shift in the relative intensity values were observed in almost all the coatings: the variations being more pronounced at the lower diffraction angles (2θ values).

   iii) No direct relationship with this deviation in intensity values from the standard values could be found during the experiments: however the following reasoning may have some relevance or bearing on the findings.

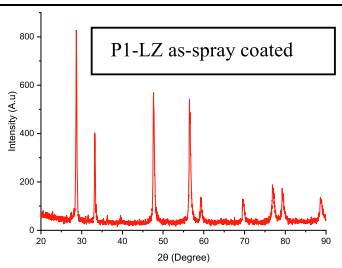
The intensity of the X-ray diffraction patterns depend on two criteria (a) the elemental composition of the materials and (b) material synthesis conditions. In this research work the three plasma sprayable powders, though of different compositions, were plasma sprayed under three identical conditions of plasma spray parameters. They include (a) voltage (b) current (c) power (d) primary gas, Ar (e) secondary gas, H_2 (SLPM) (f) power feed rate (g/min) and (g) plasma spray distance (mm). Since the preparation methods were identical, the plasma spray parameters appear to have a dominating role on the coating quality and thereby their performance as well.

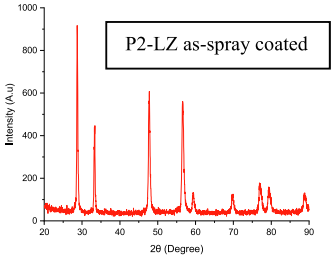
During the coating preparation process, the crystallites may take a certain direction for their growing and this most likely has been influenced by the plasma spray parameters. The many factors that have controlled the deposition during plasma spraying appears to have affected the diffraction line intensity and thereby the microstructures.

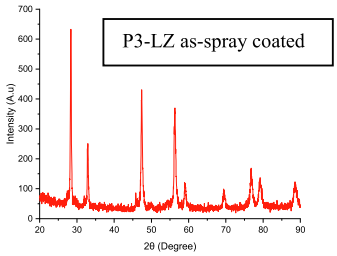
Considering all the above results the following conclusion may be drawn.

5. Conclusion

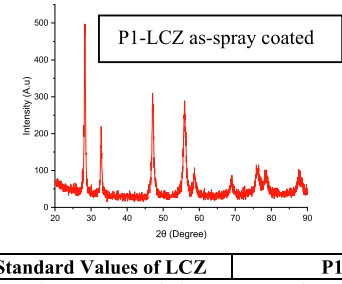
Pyrochlore Zirconate based thermal barrier coating compositions namely Lanthanum Zirconate, Lanthanum Cerium Zirconate and Lanthanum Cerate were synthesized via Atmospheric Plasma

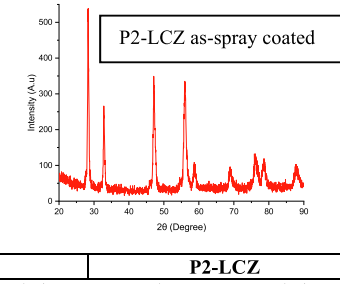


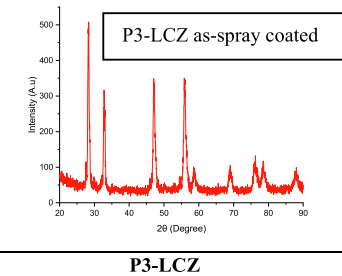




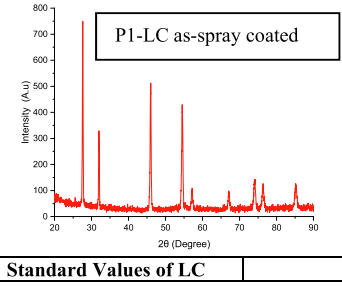
Standard Values of LZ		P1-LZ		P2-LZ		P3-LZ	
d spacing	Relative Intensity	d spacing	Relative Intensity	d spacing	Relative Intensity	d spacing	Relative Intensity
3.1208	100	3.10915	100	3.10229	100	3.14477	100
2.7027	30.4	2.69356	52	2.69016	54.09	2.71831	34.67
1.9111	47.2	1.90594	71.2	1.90338	68.69	1.91658	62.23
1.6298	40.6	1.62623	62.58	1.62413	62.88	1.63359	59.28
1.5604	9.2	1.55742	12.45	1.55567	11.61	1.56339	13.63
1.3513	6.3	1.34834	12.63	1.34746	10.18	1.35164	8.42
1.2401	15.4	1.23791	18.54	1.23655	15.89	1.24054	19.7
1.2087	12.2	1.20661	14.06	1.20529	12.95	1.2094	13.94
1.1033	11.6	1.10154	12.3	1.10066	10.27	1.10281	11.84

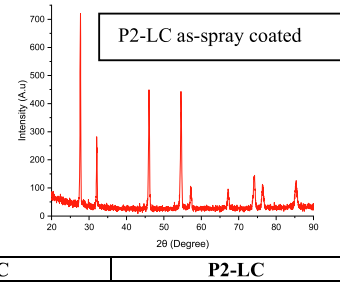


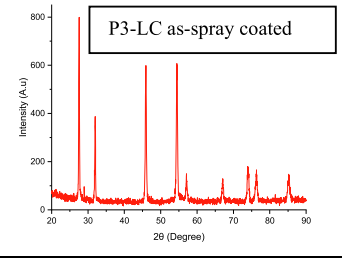




Standard Values of LCZ		P1-LCZ		P2-LCZ		P3-LCZ	
d spacing	Relative Intensity	d spacing	Relative Intensity	d spacing	Relative Intensity	d spacing	Relative Intensity
3.1459	100	3.15343	100	3.14207	100	3.13979	100
2.7245	31.1	2.72879	35.11	2.71966	45.97	2.72112	51.84
1.9265	47	1.92625	53.38	1.92318	61.07	1.92371	59.91
1.6429	41	1.64148	48.32	1.64246	70.27	1.64167	58.18
1.5729	9.3	1.57216	11.53	1.5695	12.56	1.57194	9.91
1.3622	6.4	1.36242	8.15	1.36016	10.75	1.35992	10.19
1.25	15.5	1.24984	14.12	1.24994	20.29	1.24926	14.4
1.2184	12.4	1.21928	11.82	1.21818	15.76	1.21644	11.35







Standard Values of LC		P1-LC		P2-LC		P3-LC	
d - spacing	Relative Int.	d - spacing	Relative Int.	d spacing	Relative Int.	d - spacing	Relative Int.
3.2118	100	3.22748	100	3.22099	100	3.23585	100
2.781	31.1	2.7939	39.97	2.78898	38.06	2.79953	46.82
1.966	45.6	1.9741	67.84	1.97154	65.93	1.97672	79.26
1.677	36.7	1.68315	63.62	1.6813	66.82	1.68497	82.78
1.605	7.5	1.61148	9.95	1.60977	12.17	1.61317	11.79
1.39	5.6	1.39484	10.04	1.39322	9.01	1.39577	11.69
1.276	12.3	1.27984	17.58	1.27893	19.21	1.28014	15.97
1.2439	4.4	1.2474	13.83	1.24674	13.67	1.24806	14.81
1.1355	9.4	1.13885	13.88	1.13778	13.25	1.13881	13.05

Fig. 3. XRD patterns and data corresponding to coating sprayed by using each spray parameter.

Spraying under three different plasma spray parameters. The three plasma sprayable powders were prepared under identical conditions.

The coatings were analyzed for their performance under thermal shock cycling conditions. An attempt was made to relate the test results with their crystalline phase structure and microstructures. While the microstructures gave distinct evidence of their quality (good or poor) which could be related with the performance, no direct co-relation between the diffraction patterns obtained from the various coatings and performance was possible. The variations in the diffraction intensity lines were likely attributable to the plasma spray parameter factors that have controlled the deposition

during plasma spraying (preferential orientation of certain crystallographic planes) appears to have affected the diffraction line intensity and therefore the performance as well.

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RESEARCH ARTICLE

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Thermal Shock and Oxidation Stability Tests to Grade Plasma Sprayed Functionally Gradient Thermal Barrier Coatings

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ABSTRACT: Functionally graded layers in thermal barrier coatings reduce the stress gradient between the overlaid ceramic coatings and the underlying metallic component. Introduced to alleviate early onset of spallation of the coating due to thermal expansion mismatch, this facilitates improvement in the life of the component. Conventional thermal barrier coatings typically comprise of duplex layers of plasma sprayed 8% yttria stabilized zirconia (ceramic) coatings on bond coated (NiCrAlY) components/substrates (Inconel 718 for example). This work highlights the superiority of plasma sprayed coatings synthesized from blends of the intermetallic bond coat and ceramic plasma spray powders on Inconel 718 substrates in three-layer configuration over the duplex layered configuration. Assessed through (a) thermal shock cyclic tests (at 1200°C and 1400°C) in laboratory scale basic burner rig test facility and (b) oxidation stability test in high temperature furnace (at 800°C and 1000°C) the functionally graded coatings of certain configurations exhibited more than double the life of the conventional 8% yttria stabilized zirconia duplex (double layer) coatings. Micro- and crystal structure analysis support the findings and results are detailed and discussed.

Keywords: Thermal Barrier Coatings, Functionally Gradient Materials, Plasma Spray

1. Introduction

1.1 Thermal Barrier Coatings

Thermal Barrier Coatings (TBCs) are ceramic materials, applied on metals to make their surfaces thermally insulating and to protect them from thermal degradation. Applied in the form of either thin (200–500µm) or thick (> 1 mm) coatings, industrial applications of TBCs are vast and varied such as in gas turbine, diesel, and aircraft engines [1,2]. TBCs in general, protect aerospace components from degradation at their high service temperature (>1000°C) environment, extend life and which in turn increase the performance efficiency of the aircraft engines. Typically, TBCs thicknesses are in the range of 120µm - 250µm which are comprised of low thermal conductivity material layer with suitable adhesion characteristics and microstructures [3,4]. Conventional TBC is applied to achieve adhesion of ceramic top coat over the metal component's surface through double layered coatings, namely, bond coat and ceramic top coat. The bond coat is an inter-metallic coating, 50 µm – 120 µm thick, applied above the pre-prepared metallic component surface, which develops an adhesive layer over the surface for the ceramic coating to bond. It also provides relief from the damage caused by the thermal expansion mismatch between the metal substrate and ceramic over layer [5].

Atmospheric Plasma spraying (APS) is a well-established method to fabricate TBCs with yttria (usually 8% Y_2O_3) stabilized zirconia (ZrO_2) and NiCrAlY bond coat (BC) configuration. Popularly known as 8YSZ TBCs, they possess low thermal conductivity, suitable microstructure, thermal fatigue characteristics, mechanical properties and provide protection from damage due to oxidation at high service temperature [6,7]. TBCs protect the metal substrate and parts from thermal degradation (oxidation) and therefore increase their thermal fatigue life. However, large differences in the thermal expansion characteristics of the ceramic materials and underlying base metal results in poor adhesion between the metal ceramic interface especially in service at high operating temperatures [8]. In addition to oxidation, stress buildup between the ceramic coated layers and at the interface contribute further to the adhesive failure and sometimes within inter-ceramic layers known as cohesive failure.

8YSZ is the currently the most popular TBC system. The Stabilization of the m-ZrO_2 (unstabilized monoclinic zirconia) with a dopant is carried out to stabilize the stable t-

ZrO_2 (stabilized tetragonal zirconia) at room temperature. This is because unstabilized m-ZrO_2 transforms into tetragonal ZrO_2 at temperatures above 1000°C and this is a temperature related reversible transformation. The transformation is accompanied by a reversible volume change of about 3–5%, when cycled between room temperature and at temperatures above 1000°C, resulting in their spallation. Therefore, the transformation is suppressed and the high temperature tetragonal/cubic (t/c) ZrO_2 phase is stabilized at room temperature, which eliminates the spallation due to thermal expansion issues. While the thermal conductivity of 8YSZ is suitable for gas turbine TBCs applications, this material also suffers by being prone to sintering above 1200°C, resulting in an increase of the thermal conductivity at those temperatures making the TBC less effective. Furthermore, there is reduction in tolerance to thermal stresses and the associated strains due to the sintered and densified coatings. These effects can reduce the TBCs durability to a large extent and raise adhesion issues at and above 1200°C [9,10].

The problem described above can be overcome to an appreciable extent by processing the TBCs in suitably tailored different layers, encompassed of material (ceramic and bond coat i.e. 8YSZ and NiCrAlY respectively) layers with gradually varying thermal expansion characteristics. This is done via combination of two or more different types of coating materials, with optimized coating characteristics [11,12]. The formation of layers with different thermal expansion characteristics are achieved by providing intermediate layers sandwiched between the base bond coat (BC) and the final top coat (TC). They are comprised of blends of the BC and TC. Thus, with this new concept of composite having gradual compositional and/or micro-structural variation over definable geometric orientations and by distances, three or multilayered functionally graded materials (FGM) are obtained which significantly improve the double layered 8YSZ TBCs characteristics [13,14].

The usage of FGM configurations is expected to reduce delamination remarkably within the inner layers. Even in the FGM system the ceramic layer, being the outermost layer is exposed to the harsh environment (at high temperatures) and provides the maximum protection. However, the ceramic does not end abruptly: rather being blended with bond coat, the layers below the ceramic experience gradual compositional change from being rich in ceramic to being rich in metal as moving towards the component interior [15,16]. Thus, in FGM systems, there is a strong potential for decreasing damage due to mis-match in properties amongst the TBC and the substrate. This is because the interfacial layers allow smooth transition of properties and possess higher fracture toughness. Hence a TBC built in FGM configuration is expected to be more resistant to delamination and exhibit higher durability characteristics compared to conventional TBC. Depending upon application, the gradient (or the graded) layer can be classified on basis of different parameters. They may be (a) microstructural (b) multilayers of metals, ceramics or (c) comprised of layers integrated with different densities/porosities etc., [17]. In conventional TBC system, initially the bond coat (NiCrAlY) is coated to the desired thickness on the prepared metal substrate and next, layers of the ceramic coats (say 8YSZ) are applied on the top up to the desired or the most technically feasible thicknesses.

1.2 Functionally Graded Materials

Functionally Graded Materials (FGMs) can be synthesized in different ways. The most accepted method uses pre-alloyed feedstock powders to plasma spray the desired compositions [16]. The feed stock powders are generally synthesized by weighing the desired proportions of the bond coat and ceramic top coat (e.g. 25-75 or 50-50 ceramic-bond coat blend ratio etc.), blending, ball milling the blended powders followed by plasma sphperiodization by plasma spraying into water by using the plasma torch. These powders are used as the feed stock for plasma spray coating. Using pre-alloyed feed stock powders offers several advantages: high deposition, more uniform coating density and improvement in chemical homogeneity [16].

Another method also involves blending of the constituent powders such as the bond coat and ceramic top coat in desired proportions [18]. However, the blends are directly plasma sprayed to form the coatings/FGM intermediate layers. This method although simpler, is likely to be associated with in-homogenous composition to some extent, within the same layer at different locations. A small variation to this process involves utilizing more than one torch at the same instance of spray coating, but the challenge lies in dictating the spray parameters to obtain uniform and consistent coated layers. The challenges in both these methods may be ascribed to the difference in densities, sizes, melting points and flowability possessed by the two kinds of spray powders [19]. While the superiority of pre-alloyed feed stock powders is unchallengeable, the process is relatively more expensive and technology driven than the simpler blended mixtures used as plasma spray powder. The effects of interaction between the particles and homogenization of particulate FGM in blend configuration, where the participating materials have significant variation in properties, cannot be overlooked. Nevertheless, this method is sufficient and useful to make preliminary assessment of the advantages of any one or more blended pattern over the base material. Upon establishing the most suited blend configuration, that particular FGM may be synthesized by pre-alloying the feedstock powder prior to plasma spraying [16, 20]. It is well known that FGM needs collaboration, involving more industries and international alliance to achieve the desired milestones to develop an industrial product, although small advancements in

understanding the concepts may be highly beneficial to the research community.

In addition to producing the FGMs, there is a strong need in terms of quality, reproducibility, reliability. The test methods involve the physical, chemical and mechanical behaviour of the FGMs and their correlation to the microstructure and their formation mechanism to control the fabrication process. Thus characterization plays an important role in the FGM development which should also match with the application envisaged.

Keeping this information in view, the current work focuses on the formation of FGMs by using the NiCrAlY inter-metallic bond coat and 8YSZ ceramic top coat plasma sprayable powders in different combinations of proportions, in form of blends prior to plasma spray coating on aerospace alloy substrates. Considering the FGMs are Thermal Barrier Coatings, thermal tests were performed to evaluate their characteristics. Comparisons were drawn with the duplex 8YSZ conventional TBCs as the baseline material.

2. Experimental procedure

2.1. Plasma Sprayed Coatings

Nickel based aerospace related super alloy (Inconel 718) base plates were used as substrates to synthesize the various configurations of FGMs in this work. AMDRY 962 (NiCrAlY) and METCO 204NS (8% YSZ) plasma sprayable powders were used as the bond coat (BC) and top coat (TC) respectively.

The two types of substrate plates used were (a) 50 mm X 10 mm X 5 mm: for oxidation stability test and (b) 80 mm X 75 mm X 5 mm: for thermal shock tests.

The substrates were blasted with alumina grits, de-greased with a solvent following which bond coat was deposited on the surface over prior to the plasma spray coating of the FGM layers. The coatings were synthesized by using robot controlled Atmospheric Plasma Spray (APS 100 KW Metco Sulzer) facility. Table 1 shows APS parameters for the bond coat and ceramic powder. All blends were spray coated by using spray parameters for the ceramic.

Table 1. APS parameters.

Parameter	NiCrAlY (BC)	8YSZ (TC)
Primary gas, Ar (l/min)	57	38
Power feed rate (gm/min)	45	35
Secondary gas, H_2 (l/min)	14	17
Voltage (V)	75	70
Current (A)	400	550
Spray distance (mm)	10	10

2.2 Coatings Configuration

The design configuration of the coatings that were prepared is listed in Table 2

All the coated layers were plasma sprayed onto the prepared substrates. The details of the design configuration (reflected in Table 2) are described as the following

(a) Conventional:

(i) First coated layer on grit blasted surface: Bond coat (BC) : 75 µm thick

(ii) Second coated layer on bond coated surface: Top coat (TC): ~250 µm thick (Final layer)

(b) Functionally Graded Materials (FGM) Configuration:

(1) FGM 1 configuration:

(i). First coated layer on grit blasted surface: BC: 75 µm thick

(ii). Second coated layer) on bond coated surface: blend of 25BC+75TC: ~100 µm thick (intermediate layer)

(iii). Third coated layer over intermediate layer surface: TC ~ 150 µm thick (Final layer)

Table 2. Coating Configuration (blend percentage & coating thickness)

Designation	Blend Configuration (weight %) (BC+ TC)	Thickness (µm) (BC)	Thickness (µm) Blend	Thickness (µm) (TC)
Conventional TBC	Nil	75 µm	Nil	250 µm
FGM 1	25BC + 75TC	75 µm	100 µm	150 µm
FGM 2	50BC + 50TC	75 µm	100µm	150 µm
FGM 3	60BC + 40 TC	75 µm	100 µm	150 µm

FGM 2 configuration:

(i) First coated layer on grit blasted surface: BC: 75 μm thick

(ii) Second coated layer on bond coated surface: blend of 50BC+50TC: ~ 100 μm thick (intermediate layer)

(iii) Third coated layer over intermediate layer surface: TC ~ 150 μm thick (Final layer)

(3) FGM 3 configuration:

(i) First coated layer on grit blasted surface: BC: 75 μm thick

(ii) Second coated layer on bond coated surface: blend of 60BC+40TC: ~ 100 μm thick (intermediate layer)

(iii) Third coated layer over intermediate layer surface: TC ~ 150 μm thick (Final layer)

The blends were prepared according to design ratio shown in Table 2 by weighing the bond coat (NiCrAlY) and the top coat (8YSZ) plasma sprayable powders separately. While mechanical mixing may not be the best method to synthesize a homogenous blend, this method was considered suitable to make a preliminary assessment of the concept of FGM. The identified powders and the composition of the two powders to form the blend were mixed manually for an hour right before the spray process. This was done to minimize the negative effects of segregation due to variable densities of the constituents. The intermediate blend powders thus prepared were then plasma spray coated on the bond coated surfaces by using a single plasma torch. Details of tests performed on the spray coated substrates are given below

2.3 Thermal shock (fatigue) Test.

Thermal shock cycling test emphasizes on ceramic coating surface being subjected to heat at high and low temperatures (interchanged) to observe the changes in the coating characteristics and degradation/failure occurrences caused by stresses especially due to thermal expansion. Generally some variations in the test methods have been practiced by various researchers [21]. The main methodology of test however, is generally based on standard and established ASTM tests, e.g. ASTM D 6944 - 15 [22].

Thermal cycling forms one of the few highly important deciding factors to determine the life time for the TBCs under service conditions involving high temperatures. In the present work, the outermost layer (ceramic) surface was exposed to a source of heat suddenly, to reach a prefixed high temperature (1200°C and 1400°C in this case), held at that temperature for a prefixed time before removing the heat source: followed by exposure to a cooling medium for a prefixed time. The heating source was an oxy-acetylene flame, the source to cool the hot ceramic surface was 'forced air' in ambient room temperature (~25°C) and the holding times at the time of rapid heating and rapid cooling were 60 seconds each time. This entire process of rapid heating, holding and rapid cooling comprised of one test cycle. The ceramic coating surface temperature was measured using a non-contact infra-red thermometer gun.

Severe thermal stresses are expected to be induced in the coating during the thermal shock cycling test process. Stresses are expected to be produced due to the mismatch in the thermal expansion characteristics between the top coat, and the metallic bond coat. The capability of the intermediate layers in alleviating the stresses and to prolong the life of the TBC system was being explored in this work.

2.4 Oxidation Stability Test

Oxidation stability characteristics help to understand the influence of oxidation on the underlying metal below the TBCs. In addition to the increased oxygen ionic conductivity at high temperatures (>800°C), porosities in the coatings play an important role in oxygen transport through them and thereby significantly influence the metal substrate degradation. Therefore, in order to extend the life of the component on which TBC is applied, not only should there be good adherence between the bond coat and top coat but also must be synthesized with optimum porosity for best (low) thermal conductivity and minimum oxygen transport characteristics. In service, due to prolonged heating there is a progressive change in area of contact between the bond coat and top coat due to the formation of thermally grown oxide (TGO) [23,24]. Increased oxidation transport is not desirable in these systems and it is important to control the growth of TGO. Reportedly [25, 26] TGO, when allowed to grow beyond a threshold value of 6-7 μm, exerts severe compressive stresses on the overlaid coatings, resulting in tensile stresses in the ceramic layers of which therefore are unable to remain intact and flake off. The study of the influence of the FGM microstructure in controlling the porosity in the microstructure and the oxidation characteristics as well was attempted in this work.

To carry out the oxidation stability test, Inconel718 test bars of dimension 50 mm X 10 mm X 5 mm were coated on all sides as per the design configuration (Table 2) and tested at 800°C and 1000°C by employing a muffle furnace. The coated test bars were introduced into the high temperature furnace at ambient temperature and gradually rising the temperature of the furnace to the required temperature and holding for 12 hours followed by furnace cooling to normal ambient temperature inside the furnace. The specimens was removed and examined with naked eyes or under low power magnification (10X) for any defects. If the coatings were damaged (cracked, peeled off or degraded) the test was stopped. If not, the cycle was repeated until the coating on the specimen showed signs of damage.

2.5 Characterization

2.5.1 Microstructure and Structural phase analysis

Scanning Electron Microscope (SEM) was employed to analyze the metallographic polished cross sections removed from the as-sprayed specimen and those subjected to thermal tests. The substrate-coating interface and its microstructure were examined in detail. X-ray diffractometer (XRD) was used to carry out the structural phase analysis of the coated specimens.

3. Results

3.1 Microstructure of As-sprayed Coatings

Fig 1 shows the microstructures of as sprayed coatings of (a) Conventional 8YSZ (b) FGM 2 (typical) TBCs when studied in polished cross section metallographic specimen.

(a) Conventional Coating: ~ 65 µm thick bond coat ~310 µm thick top coat (YSZ) was measured from the SEM micrograph (Fig 1a).

3.2 Thermal shock (fatigue) test performances of Conventional and FGM TBCs

In this test, the thermal fatigue characteristics of the sample and the number of thermal cycles (heating and cooling cycles) through which the sample have gone through has been highlighted in Table 3 and Table 4 shows the summarized results of thermal shock test at 1200oC and 1400 oC.

From these results it is observed that an introduction of FGM layer between the bond coat and ceramic coat layers in TBC shows high potential in extending the life of duplex coatings under the thermal shock cycles test conditions adopted in this work. The other parameters such as thermal conductivity, mechanical stresses associated with the introduction of an intermediate third layer warrants detailed investigation though.

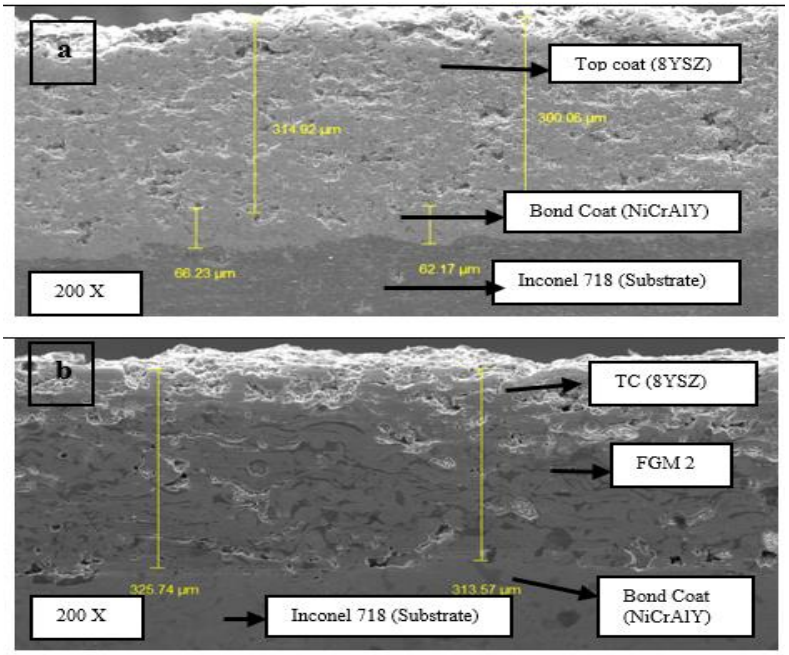

Fig 1. SEM image of As-sprayed cross-sectioned specimen: a) Conventional TBC; b) FGM 2 TBC

Table 3. Results of Thermal Shock Test at 1200°C

S.No	Specimen Designation	Bond Coat BC(µm)	Blended Configuration Wt %(BC+(C)) (µm)	Top coat (C) (µm)	Number of cycles	Remarks
1	Conv TBC	75	---	300	156	Failed
2	FGM 1	75	150	150	162	Failed
3	FGM 2	75	150	150	182	Not Failed (Test Stopped)
4	FGM 3	75	150	150	170	Not Failed (Test Stopped)

Table 4. Results of Thermal Shock Test at 1400°C

S.No	Specimen Designation	Bond Coat BC (µm)	Blended Configuration Wt %(BC+ TC) (µm)	Top coat (C) (µm)	Number of cycles	Remarks
1	Conv. TBC	75	---	300	182	Failed
2	FGM 1	75	150	150	174	Failed
3	FGM 2	75	150	150	210	Not Failed (Test Stopped)
4	FGM 3	75	150	150	184	Not Failed (Test Stopped)

Table 5. Findings from the XRD patterns

Sl No.	Reference in Fig 2	Sample Details Thermal shock cycling @ 1200°C (XRD on outer most surface)	Findings from XRD pattern	Remarks
1.	a	Conventional as-sprayed	(%) c/t-ZrO_2 = 100	No destabilization
2.	b	Conventional – Failed (156 cycles)	(%) c/t-ZrO_2 = 100	No destabilization
3.	c	FGM 1 – Failed (162 cycles)	(%) c/t-ZrO_2 = 98 (%) m -ZrO_2 = 2	Mild destabilization
4.	d	FGM 2- Not Failed (182 cycles)	(%) c/t-ZrO_2 = 84 (%) m -ZrO_2 = 16	Significant destabilization
5.	e	FGM 3- Not Failed (170 cycles)	(%) c/t-ZrO_2 = 94 (%) m -ZrO_2 = 6	Moderate destabilization

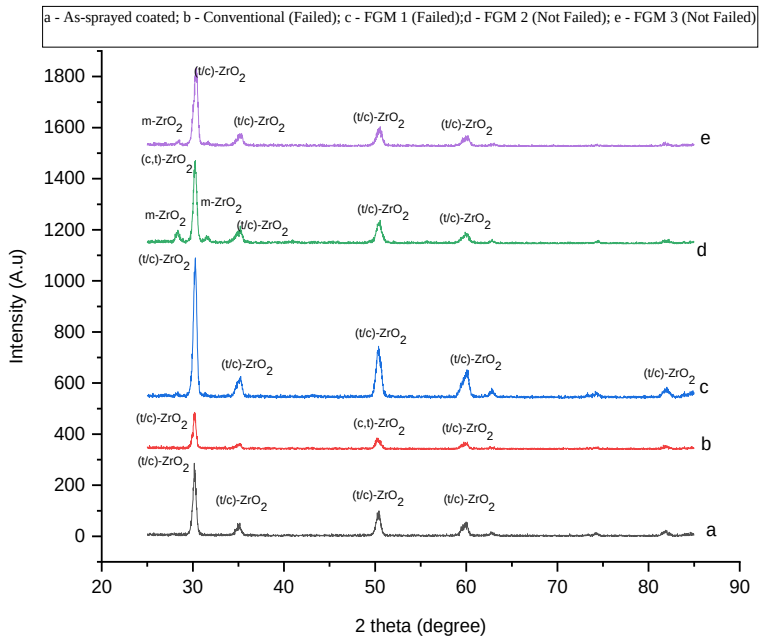

Fig 2. XRD patterns of thermal shock specimen of conventional and various FGM configurations at 1200°C

3.3 X-Ray Diffraction Analysis on thermal Shock tested specimen

The XRD patterns of as-sprayed coated and thermal shock test specimen of conventional and various FGM configurations at 1200°C is shown in the Fig 2. Table 5 shows the findings from the XRD patterns shown in the Fig 2. Table 5 shows the findings from the XRD patterns shown in the Fig 2

3.4 Oxidation stability Test

The results obtained after conducting oxidation stability test on conventional and FGM blended configuration, at 800°C are shown in Fig 3: shows (a) the conventional TBCs samples failed in 96 hours of test and (b) blended configuration (FGM 1, FGM 2 and FGM 3) not failed even after 264 hours of testing. Similarly, the specimen also underwent oxidation stability test at 1000°C. Results are shown in Fig 4.

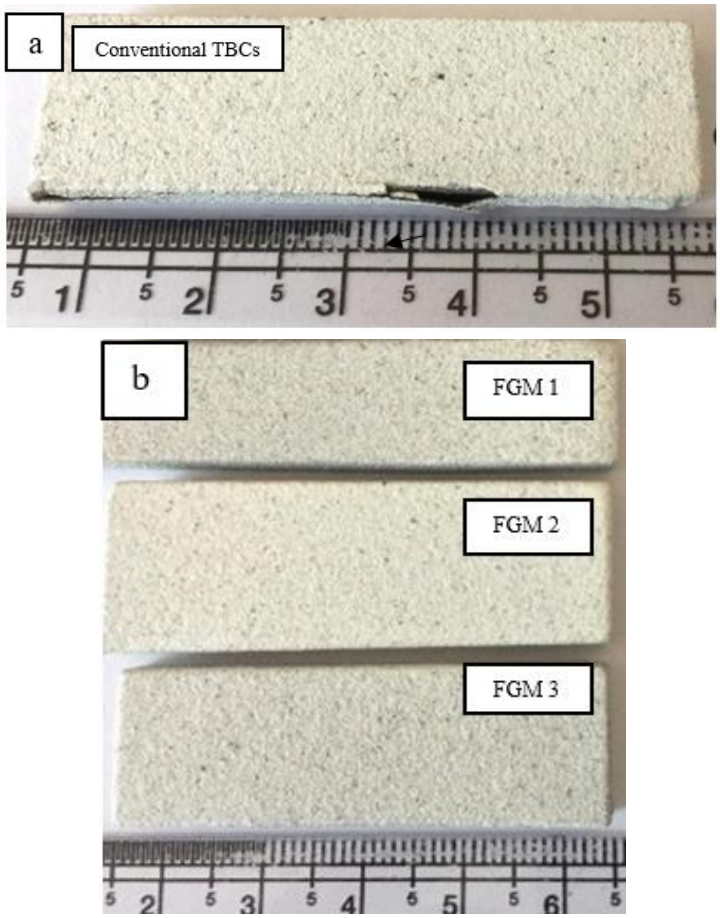

Fig 3. Oxidation stability tested specimens at 800°C:a) Conventional TBCs specimen, failed at 96 hours; b) FGM TBCs specimens after 264 hours (without cracks on the surface)

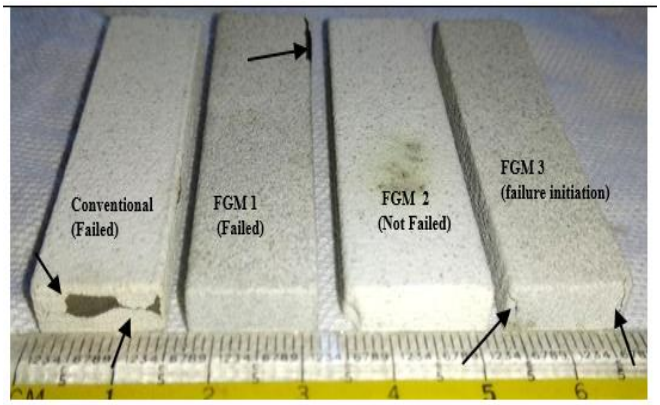

Fig 4. Oxidation stability tests at 1000°C (arrows show the failure location on the surface) [28]

Table 6. Results from oxidation stability tests (Conventional & FGM specimen) at 800 and 1000°C

S.No	Specimen Designation	No. of hours at 800°C (Cycles)/remarks	No. of hours at 1000°C (Cycles)/remarks
1	Conv TBC	96 (8)/Failed	24 (2)/ Failed
2	FGM 1	264 (22)/ Not Failed	60(5)/ Failed
3	FGM 2	264 (22)/ Not Failed	72 (6)/ Not Failed
4	FGM 3	264 (22)/ Not Failed	72 (6)/ Not Failed*

* Apparent failure due to specimen sharp edge

Table 6 shows the summarized results of oxidation stability tests at 1000°C. The improvement showed by TBCs in the functionally graded materials configurations over conventional TBCs at high temperatures is revealed.

3.5 Cross sectional metallography (SEM) after oxidation stability test

`Microstructure analysis was performed on cross section metallographic specimen removed from specimen of conventional 8YSZ and FGM configurations that had undergone oxidation stability test at 800 and 1000°C. The specimen were examined under SEM with EDS facility.

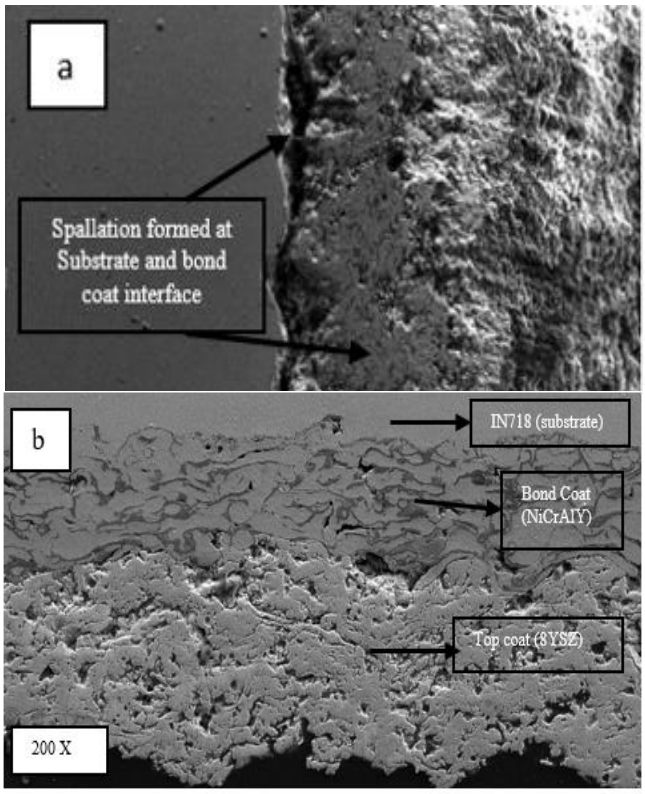

Fig 5. SEM micrograph of cross section metallographic specimen after oxidation stability test: (a) Conventional 8YPSZ tested at 800°C failed at 96 hours; (b) Conventional 8YPSZ tested at 1000°C failed at 24 hours

Fig 5a shows a micrograph of the conventional 8YSZ specimen that has undergone oxidation stability test at 800°C for 96 hours. Characterized by severe delamination between the substrate and the bond coat, the specimen in this system failed within 96 hours of test. The top coat of the specimen in this system when subjected to oxidation stability test at 1000°C for 24 hours, which failed (shown in Fig 5) revealed largely a porous structure (Fig 5b). Microstructure of the as-sprayed coating (shown in Fig 1 a) was devoid of such porosity.

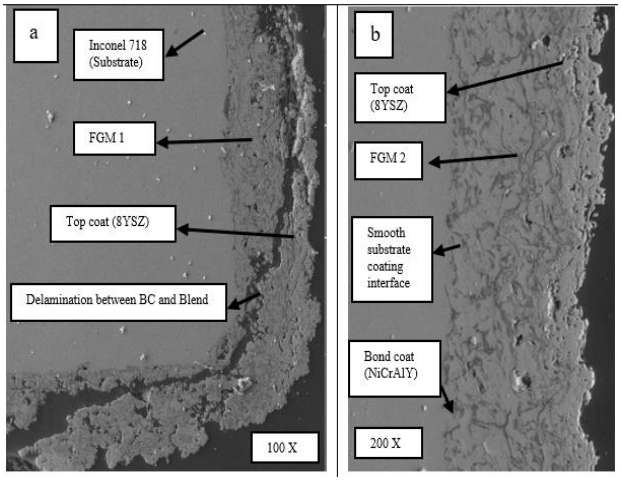

Fig 6. SEM micrographs of FGM TBCs (polished metallographic cross section) after oxidation stability test at 1000°C. a) FGM 1 b) FGM 2

SEM analysis was performed on metallographic specimen of cross section of FGM specimens (oxidation stability tested at 1000°C). SEM micrograph of FGM 1 failed in 60 hours and FGM 2 not failed after 72 hours of oxidation stabiliy tests are shown in Fig 6 a and 6b respectively.

It is observed that detachment or delamination of layer (shown in Fig 6a (FGM1)) is formed between the blend and the ceramic top coat is due to the thermal expansion mismatch. Whereas, FGM 2 withstood 72 hours without failure signs on the surface under the same conditions is shown in Fig 6b. A certain level of surface roughness is observed due to metallography polishing of the coating.

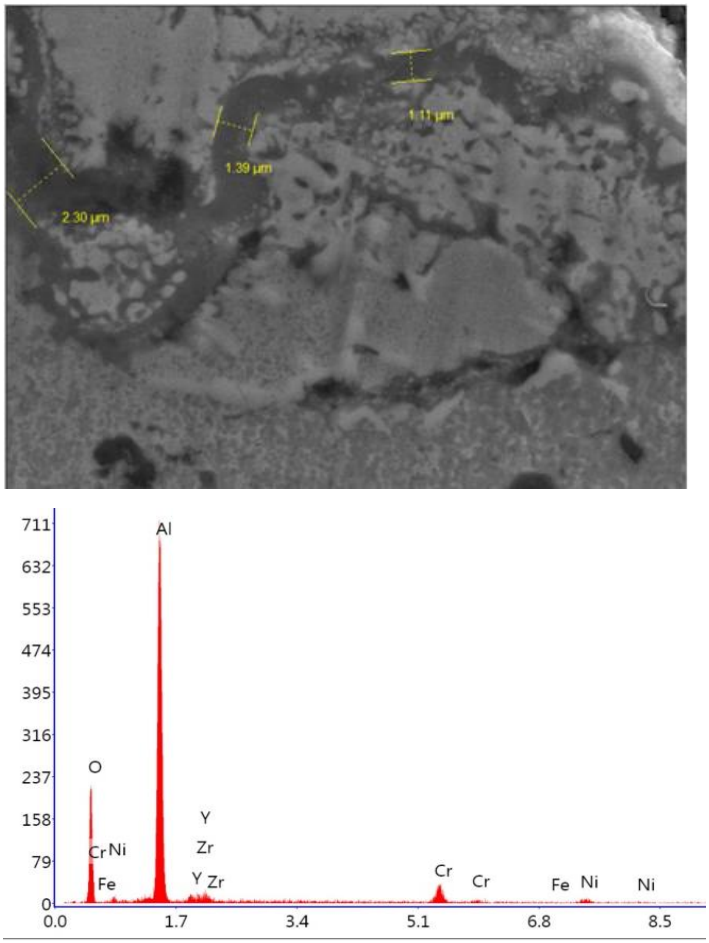

Fig 7. a) Oxide formed in between the BC and TC; **b)** EDS of conventional coating surface on selected area after oxidation test at 1000°C

Detailed examination of the cross section metallographic specimen (polished and etched) removed from Conventional TBC specimen, which was already subjected to oxidation stability test at 1000°C revealed significant oxidation within the interlayers. Fig 7a shows a typical SEM micrograph. Formation of oxide layers, ~1 to 2 µm thick, predominantly occurred between the NiCrAlY (BC) and 8YSZ (TC) layers, which pointed towards the development of thermally grown oxide TGO layers, most likely in initial stages. Confirmed via EDS analysis of on selected area of oxidation on the specimen, shown in Fig 7b, oxide scale Al_2O_3 was formed within the coated layers. This was attributable to the localized oxidation of Al resulting in the initiation of the formation of Al_2O_3, the most likely reason for the failure of the coating.

4. Discussion

The results presented here demonstrate that the blend chemistry has a significant influence on the performance of APS TBC system. According to the established theory, the primarily driving force for TBCs failure mainly comes from the mismatch stresses induced by the difference in the coefficients of thermal expansion (CTE) between the layers. The stresses may also arise from the well-known phase transformation between the tetragonal ZrO_2 and monoclinic ZrO_2 phase. However, the manner in which these stresses are relieved depends on the specific materials properties and thermal history (isothermal or cycled). Destabilization and extent of reformation of m-ZrO_2, shown in table 5 does not appear to have influenced the failure, wherever it has occurred.

A significant feature observed in the microstructures (not studied in detail in this work at this stage) of as sprayed coatings of conventional and FGM TBCs is the presence of relatively large number of porosities in the conventional TBC. Blend microstructure comprised of considerably lower porosity contents. A quantitative analysis of porosity contents is beyond the scope of this paper.

The failure mechanism of thermal shock tested conventional specimens in this work may be attributed to the thermal stresses generated between the top coat (YSZ) and bond coat: in a manner similar to results reported in TBC system by C. Giolli et.al [27]. Even in oxidation stability test, the cracking and delamination of the top coat appeared to have been generated at the bond coat top coat interface, but the failure mechanism appeared to be due to the growth thermal grown oxide (TGO) layer formed at the interface that occurred by oxidation of the NiCrAlY. This effect was similar to the findings of Khor et.al [16]. In addition, large

amount of cracks also due to coalescence of existing porosity could have been formed on the ceramic top of conventional specimen which was most likely due to the sintering effect of the ceramic. Such failures (merging of porosities) evidently did not occur in FGM configuration especially where the porosities were minimum as clearly seen in FGM 2 and possibly in FGM 3 as well (not studied).

5. Conclusions

Functionally graded and a conventional thermal barrier coating of 8YSZ and NiCrAlY were synthesized using APS system. Blends of the two plasma spray powders i.e., 8YSZ and NiCrAlY in FGM configuration exhibited superior thermal shock cycle resistance over conventional TBCs. Thermal shock tests performed on the specimen at 1200^{0}C and 1400^{0}C demonstrated the superiority of certain blend compositions. Oxidation tests performed at 800^{0}C to 1000^{0}C confirmed the findings. Failures in FGM configuration, especially in 50 NiCrAlY -50 8YSZ blend composition, most likely reduced due to lowered thermal expansion coefficient mismatch. This is attributed to the gradual change in coating characteristics in FGM configuration when both, the FGM and conventional TBCs underwent tests at the same conditions. Thus the improved performance of chosen FGM configuration over conventionally synthesized TBCs and their use in terms of thermal shock resistance and oxidation resistance is unequivocally re-established.

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Zirconia based pyrochlore thermal barrier coatings

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Abstract. Improvements in thermal barrier coatings (TBCs) technology, further than what is already in service to enable adequate protection to metallic components from higher (>1100°C) operating temperatures requires newer developments in materials. Many research activities have been undertaken by scientists to seek alternatives after discovering the threshold of Yttria-stabilized zirconia (YSZ) TBCs on standard aero-space materials at elevated temperatures. To increase the thermal performance of gas turbine engines, alternate TBC materials with better sintering resistance and lower thermal conductivity are required. One of the promising candidates for the TBCs is Pyrochlore-type rare earth zirconium oxides ($Re_2Zr_2O_7$, Re = rare earth). $Re_2Zr_2O_7$ TBCs have higher phase stability, lower thermal conductivity, lower sintering rate, no phase transformation, and lower coefficient of thermal expansion at elevated temperatures when compared with YSZ. In this work, plasma spray powders of Lanthanum Zirconate ($La_2Zr_2O_7$) and Lanthanum Ceria Zirconate (La_2 $(Zr_{0.7}Ce_{0.3})_2O_7$) were synthesized by the solid-state reaction method with the goal to develop pyrochlore oxide-based coatings with desired properties at high temperatures (>1200°C), better than the YSZ TBCs: currently the most popular choice for TBCs. These TBCs are expected to increase gas turbine efficiencies while protecting the underlying metallic substrate at high operation temperatures. The evaluation of the synthesised TBCs has been carrying out by studying their performances at 1200°C. Results of evaluation for phase composition by employing X-Ray Diffractometry (XRD), microstructure via Scanning electron Microscope (SEM) and chemical composition via Energy Dispersive spectroscopy (EDS) also have been included.

1. Introduction

Plasma sprayed thermal barrier coatings (TBC) have been used in modern gas turbines for decades to improve performance [1]. The durability of the component is increased as the thermal barrier coating layer can effectively decrease the temperature of the substance it is coated on (metal substrate). Furthermore, efficiency of the turbines can be increased as higher inlet temperatures can be used. Due to this reason TBCs provide a huge advantage in the daily functioning of aircraft engines, and gas turbines engines [2]. These TBC systems are complex: have multiple layers and materials with many varieties pertaining to composition, processing, and micro-structure. These generally have two layers: an intermediate bond coat and insulated ceramic top coat. The bond coat (NiCrAlY) is mostly inter-metallic

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and protects the metallic substrate from oxidation and corrosion [3]. It also strengthens the bond between the metallic substrate and the top coat. The ceramic top coat is able to provide heat insulation as it has low thermal conductivity.

Turbine engines when operating at high temperatures have high efficiencies, low emissions, and consume less fuel and therefore require pyrochlore oxides that have lower thermal conductivity. These are specially fabricated for advanced TBCs [4]. The corrosion characteristics along with the physical and chemical characteristics limit the performance of the base materials (super alloys, silicon-based ceramics, etc.) at high operational temperature [5]. To further increase operational temperatures of the super alloys or base metals, TBCs are applied in the form of a thin layer or coating. Currently the most commonly used material for TBC is yttria partially stabilized zirconia (YSZ) which is used for coating engine parts by the process of atomic plasma spraying (APS) or electron beam physical vapour deposition (EBPVD). The effectiveness of YSZ decreases at higher temperatures due to the effect of sintering which tends to increase the thermal conductivity [5]. The coating's durability reduces significantly when the strain tolerance and thermal stress reduces as the coatings are densified and sintered at higher temperatures: these limitations are overcome via advanced TBC materials [6].

6 to 8 by weight% of Yttria (Y_2O_3) in YSZ is the most preferred as TBC material due to its ability to resist fracture and high thermal expansion [7]. YSZ coatings are made with Atomic Plasma Spraying (APS) process; they may consist of a metastable state tδ phase. With long duration of exposure to higher temperatures, it decomposes forming stabilized zirconia phases with high or low Yttria content [8]. The zirconia with low Yttria content later gets converted into monoclinic phase with a significant increase in volume. This may be disastrous as it may lead to the failure of TBC at temperature > 1200^{o}C. Also, sintering decreases the high temperature properties as the coatings undergo a loss of strain tolerance which causes an early failure [9]. In addition, the phase stability is also limited. These drawbacks have led researchers to seek ceramic materials with much improved characteristics than YSZ. The most promising materials to be used for TBCs at high temperatures are pyrochlore-type zirconates ($Re_2Zr_2O_7$, Re = rare earth) [10]. These materials have lower thermal conductivity, high temperature phase stability, low sintering rate, no phase transformation at elevated temperatures and lower Coefficient of thermal Expansion (CTE) than YSZ.

Zirconate pyrochlores generally have lower ability to conduct heat with stability at high temperatures. Lanthanum Zirconate $La_2Zr_2O_7$ (LZ) is stable up to its melting point i.e. 2700 °C [11]. It also shows a lower sintering tendency and lower thermal conductivity (1.56 Wm-1k-1, bulk material) compared to YSZ. However since its thermal expansion coefficient is low (9.1 x 10^{-6} k^{-1} (300-1000^{o}C)) in relation to bond coats and due to poor toughness [12] pyrochlores are combined with YSZ for better use in TBC systems. YSZ is coated as the first ceramic layer since TBC failure takes place due to crack initiation occurring near the bond coat [13]. This YSZ intermediate layer potentially prevents any possible reactions between the applied pyrochlore and the thermally-grown oxide (TGO) layer formed above the bond coat when subjected to thermal load [14]. However, in the case of rapid solidification considerable amounts of metastable fluorite phases are formed which is typical in plasma spray conditions [15]. The phase transformation of fluorite to pyrochlore takes place at high temperatures (above 1000^{o}C). This transformation does not undergo a significant change in volume and is therefore not critical [16]. Since La_2O_3 is prone to evaporation in plasma spraying, the process of Lanthanum Zirconate composition by APS is still highly challenging.

2. Experimental Procedures

2.1 Powder Preparations

Commercially available raw ceramic powders used such as La_2O_3, ZrO_2 and CeO_2 (all 99.9%, Aldrich) were used in the work. The plasma spray powders of LZ and LCZ was synthesized by the solid-state method [17].Crystallographic structural phases of powders were analyzed using X-ray Diffractometer (XRD). Scanning Electron Microscope (SEM) was used to study the powder particles (morphology and particles size) of the raw and plasma spray powders of LZ and LCZ and its chemical composition was

verified by Energy Dispersive Spectroscopy (EDS) allied with SEM. The zirconia based pyrochlore (LZ and LCZ) were mixed with 10 % PVA (Poly Vinyl Alcohol) and were further processed by using standard ASTM meshes (25 mesh ~ 600 microns; 150 mesh ~106 microns; 300 mesh ~ 53 microns) [18]. Powders pertaining to -106 + 53 microns were the plasma sprayable powder which was used for plasma spray coating on the substrate.

The several steps involved in the plasma sprayable powder preparation and coating of LZ and LCZ is shown in the form of flow chart in Figure 1.

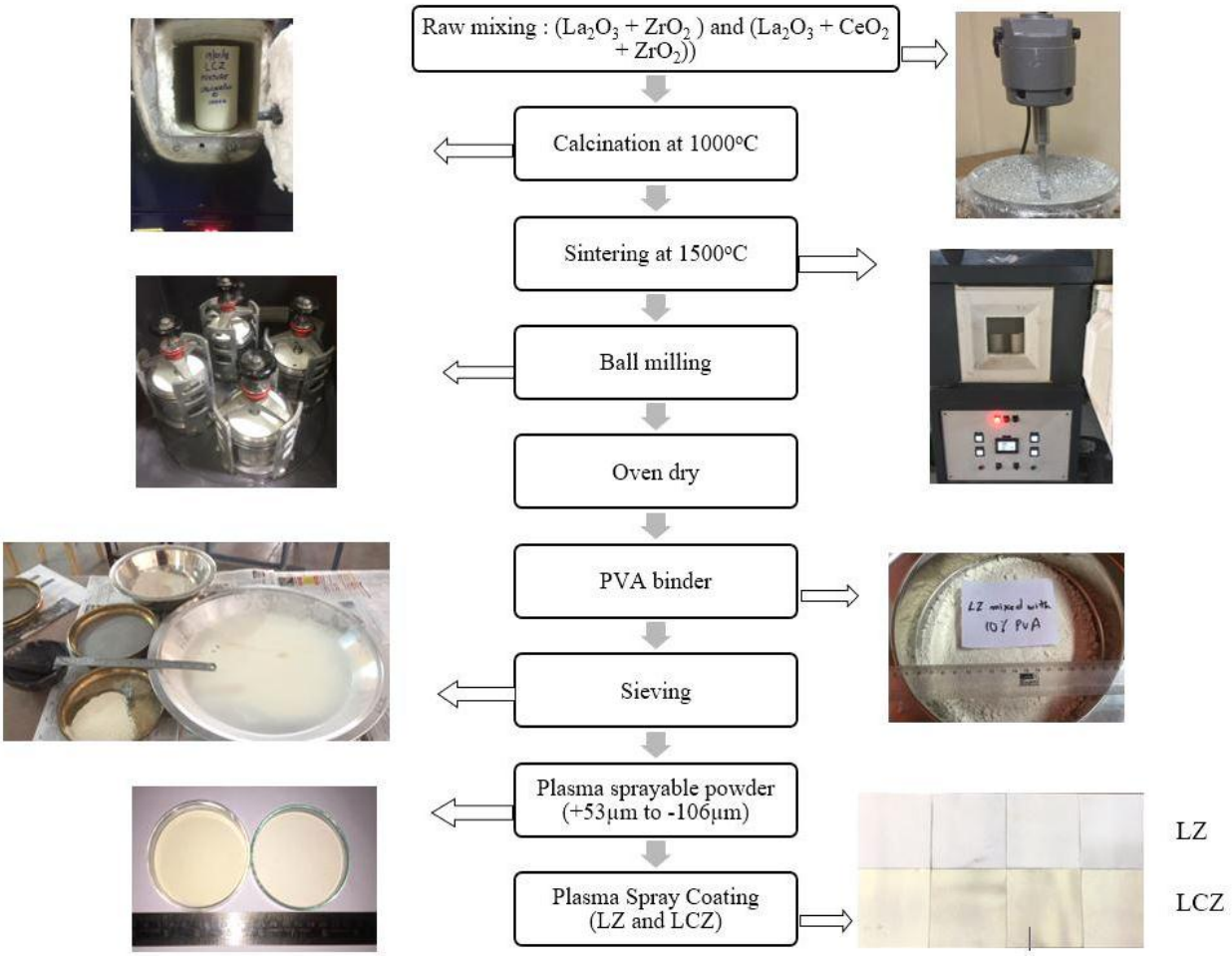


Figure 1. Plasma Sprayable Powders Synthesis (Flow chart)

2.2 Plasma Spray Coated Specimens

Nickel base super alloy (Inconel 718) were used as substrate of dimensions 80 mm x 80 mm x 5 mm (thickness). Plasma-sprayed coatings were produced by atmospheric plasma spray (APS) method with an 80 Kw Sulzer Metco Triplex gun. Commercially available Bond coat (BC)- AMDRY 962 (Ni-22Cr-10Al-1Y, -106 +52 µm), METCO 204NS (8% Y_2O_3-ZrO_2, -106+11 µm) and laboratory prepared plasma spray powder (LZ and LCZ (-106 +52 µm)) were used for plasma spray coating on the substrate.

The plasma spray parameters used in this work are given in Table 1.

Table1. Plasma Spray Parameters

Parameters	Bond Coat (NiCrAlY)	Ceramic Top Coat (LZ/LCZ)
Voltage (V)	60	55
Current (A)	400	550
Primary gas, Ar (1/min)	57	38
Secondary gas, H_2(1/min)	17	17
Power feed rate (g/min)	45	35
Spray distance (mm)	60	55
Parameters	60	55

2.3 Thermal Shock Tests

The thermal shock test involved exposing the ceramic surface to 1473K (1200^{o}C) for a pre-fixed amount of time (1 minute) and suddenly withdrawing the specimen to rapidly quench the hot ceramic surface for 1 minute. Pt-PtRh thermocouples and non-contact IR thermometers were used to measure the temperatures [19]. The numbers of such heat quench cycles were recorded to evaluate the suitability of the TBC to protect the Inconel substrate from such an extremely harsh thermal environment and further subjected to materials related metrological studies.

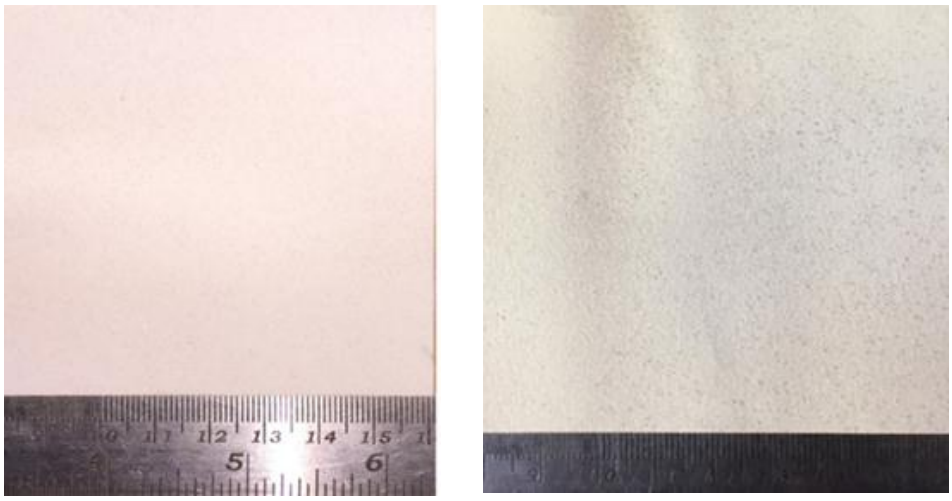
2.4 Characterization

Phase analysis of plasma spray powders and as-sprayed coatings of LZ and LCZ were carried out by using the XRD. Scanning electron microscopy (SEM) allied with energy dispersive X-ray analysis (EDXA) was used to study the microstructure and to determine the chemical composition of laboratory prepared plasma spray coatings respectively.

3. Results and Discussion

3.1 Plasma Spray Coated Specimen

Figure 2. shows the photographs of the as-sprayed coatings of LZ and LCZ plasma sprayed powders coated on Inconel718 substrates. The as-sprayed coating surfaces were uniform and smooth.

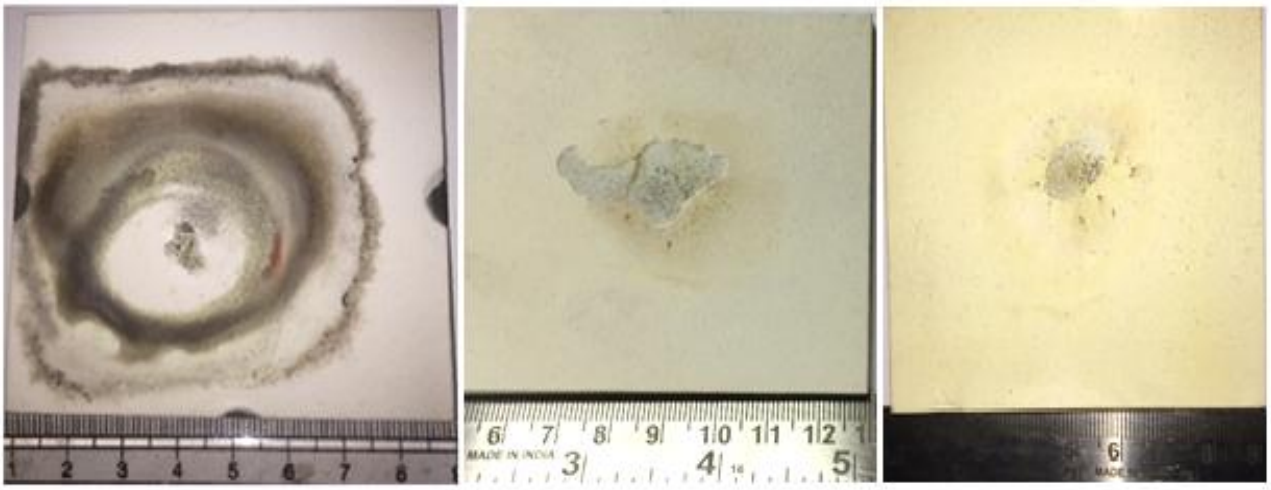


a) LZ b) LCZ

Figure 2. As sprayed coated specimens

3.2 Thermal Shock Test Results

The thermal shocked test specimen exhibited significantly varied performance and test results between the conventional YSZ, LZ and LCZ TBC's. The results pertain to the test when the hot face (ceramic surface) was subjected to the extremely harsh environment (flame surface temperature at ceramic surface 1200oC). The conventional YSZ specimen failed at the end of 90 thermal shock cycles while the specimen with LZ and LCZ failed at 170 and 210 cycles respectively. Failure was recorded when the topmost ceramic layer (visible to naked eye) either cracked or showed signs of degradation such as peeling off. These important results exhibit the highly superior characteristics in zirconia based pyrochlore TBC'S. Figure 3 shows the ceramic topmost surface of the specimen at the end of thermal shock tests at 1200^{O}C.

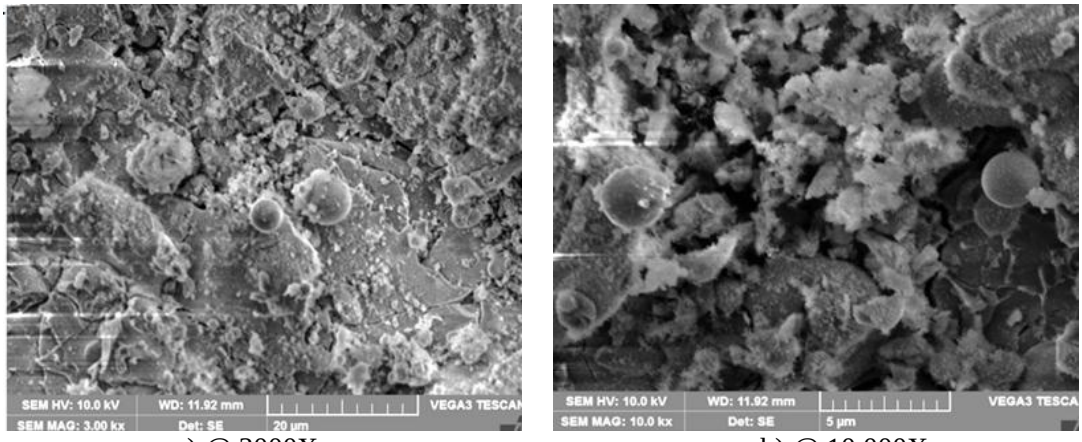


a) Conventional YSZ 1200^{o}C, failed in 90 cycles | b) Conventional LZ 1200^{o}C failed in 170 cycles | c) Conventional LCZ 1200^{o}C failed in 210 cycles

Figure 3. Specimen Thermal shock tested at 1200^{o}C (a through c)

3.3. Microstructural Analysis and Chemical Composition of LZ

Figure 4 shows the LZ plasma spray coated surface microstructure obtained by using SEM at magnifications of 3000 X and 10000 X. The grains in the spray-coated surfaces were only a few microns sized and were determined to be in the range of 1-5 microns, depicting an extremely fine-grained microstructure. Similar microstructures have been reported by other workers as well [20].



a) @ 3000X b) @ 10,000X

Figure 4. SEM Micrograph of LZ plasma spray-coated surface

SEM (EDS) was used to analyse the chemical composition on selected surface of LZ coated specimen and the EDS pattern and chemical composition is shown in Fig.5. Peaks pertaining to Lanthanum (La), Zirconium (Zr), Cerium (Ce) and Oxygen (O) were present in the EDS patterns. Figure 6 shows the chemical composition of the selected area of LZ as-spray coated specimen.

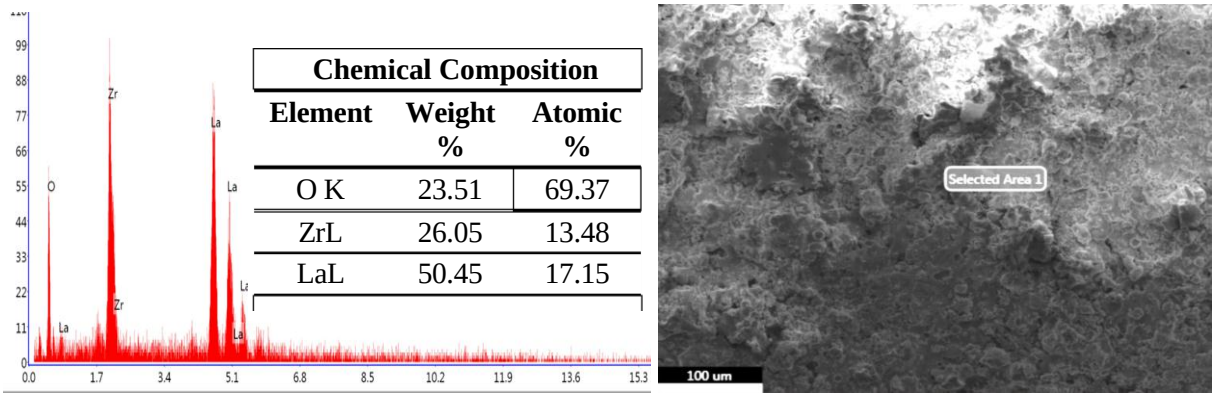


Figure 5. EDS pattern of LZ coated surface showing Elemental composition and the spray- coated surface (selected area SEM Image)

3.4. Crystallographic Structural Phase Analysis of LZ spray coated specimen

Figure 6 (a thru e) shows the XRD patterns of LZ powders and coatings that have undergone different heat treatments during processing. The changes in the patterns show the various phases formed during the various stages of processing of La_2O_3, ZrO_2 (mixing, calcination and plasma spraying). The final phase (lanthanum zirconate pyrocholore structure) has not yet formed at 1000^{o}C while a completely crystalline phase is formed at 1500^{o}C. Plasma spray processing appears to have introduced some amount of glassiness to the structure (broadened peaks) which was evident in the microstructure analysis as well. The peaks were observed to shift towards the right, which reveals the LZ formation of metastable phase

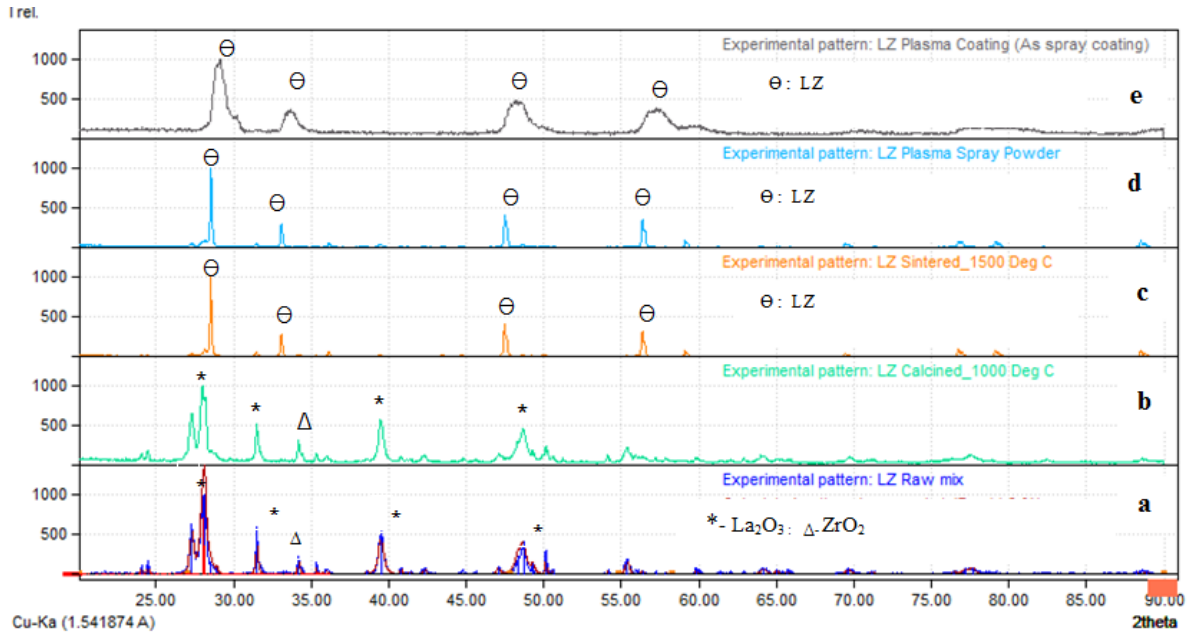
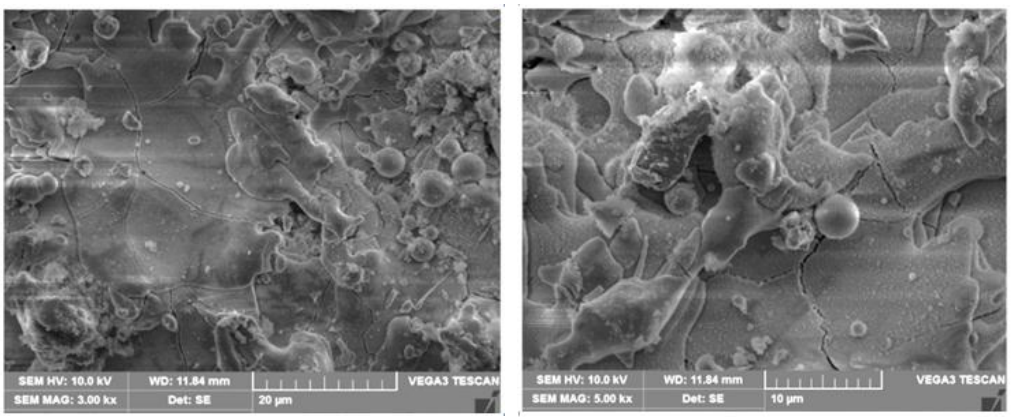


Figure 6. XRD patterns of LZ powders a) Raw mixed b) Calcined at 1000^{o}C c) LZ Sintered at 1500^{o}C d) Plasma Spray Powders e) LZ Plasma spray coated on Inconel 718 substrate.

3.5. Microstructural Analysis and Chemical Composition of LCZ spray coated specimen

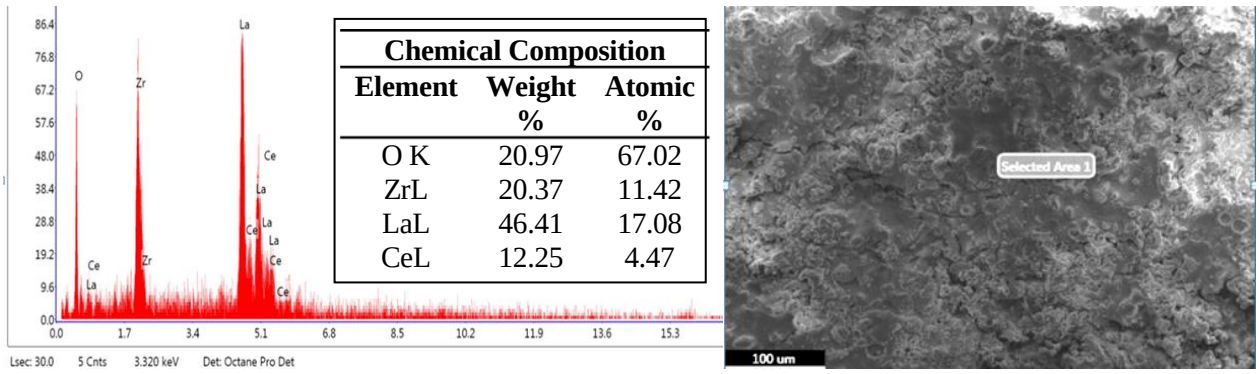
Figure 7 shows LCZ plasma spray coated surface microstructure obtained by using SEM at magnifications of 3000 X and 10000 X. The microstructure was as expected glassy, with almost 100% melting achieved via the process of plasma spray coating. The grain sizes of the melted particles on the glassy matrix of the coatings were found to no larger than the range of 1 to 10 microns, a fine grained microstructure.



a) @ 3,000X b) @ 10,000X

Figure 7. SEM Micrograph of LCZ plasma spray-coated surface

SEM (EDS) was used to analyse the chemical composition on selected surface of LCZ coated specimen which is shown in Figure 8 shows the chemical composition of the selected area of LCZ as-spray coated specimen.



Chemical Composition		
Element	**Weight %**	**Atomic %**
O K	20.97	67.02
ZrL	20.37	11.42
LaL	46.41	17.08
CeL	12.25	4.47

Figure 8. Elemental composition of SEM Image on The LCZ spray- coated surface on selected area

3.6. Crystallographic Structural Phase Analysis of LCZ spray coated specimen

The phase formation of LCZ (lanthanum ceriate zirconate pyrocholore structure) is similar to the LZ formation as discussed in section 3.4. XRD patterns of LCZ powders and coatings that have undergone different heat treatments during processing which are seen in figure 9 (a thru e). The changes in the patterns show the various phases formed during the various stages of processing of La_2O_3, CeO_2. ZrO_2 (mixing, calcination and plasma spraying) and a complete crystalline phase is formed at 1500^{o}C. The LCZ broadening peaks exhibited characteristics similar to LZ.

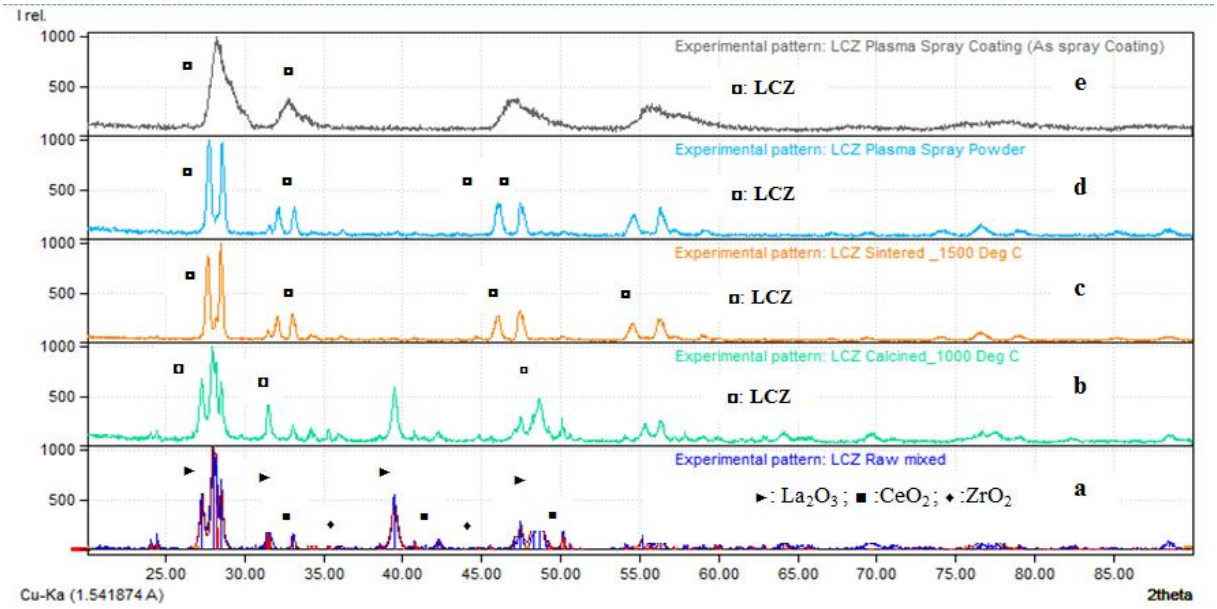


Figure 9. XRD patterns of LCZ powders a) Raw materials mixed b) Calcined at 1000^{o}C c) LCZ Sintered at 1500 ^{o}C d) Plasma Spray Powders e) LCZ Plasma spray coated on Inconel 718 substrate

4. Conclusion

Plasma sprayable powders of LZ and LCZ were synthesized from La_2O_3, ZrO_2, and CeO_2 raw material composition. Organic binder (PVA) was used to synthesis these composition by manual methods such as grinding, oven drying and different sieves mesh were used in order to get good flowability of plasma spray powders. Inconel 718 were used as substrate, bond coat (NiCrAlY) layer were sprayed followed by plasma spray powders LZ and LCZ using APS method. Crystal Structural Phase analysis, microstructure and chemical composition confirmed the presence of pyrochlore phases in the LZ and LCZ coatings. The zirconia based pyrochlore (LZ and LCZ) TBC's exhibited superior thermal shock cycle resistance over conventional Yttria stabilized TBCs.

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Synthesis and Studies on Partially Stabilized Zirconia and Rare-Earth Zirconate Pyrochlore Structured Multilayered Coatings

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Abstract

This work is focused on the thermal fatigue behaviour studies of ceramic coatings, as TBC (Thermal Barrier Coating) system, its importance in determining the thermo-mechanical properties and service-life estimation of the coatings when exposed to elevated operating temperatures. Commercial 6-8%Yttria stabilized zirconia (YSZ) top coat (TC) and NiCrAlY bond coat (BC) in (a) conventional YSZ (BC and TC), (b) multi-layered functionally graded materials (FGM) i.e., BC - blend (50BC+50TC)-(TC) configuration and (c) lab synthesized Zirconia based pyrochlore (Lanthanum Zirconate-LZ) were the coating materials involved. Nickel based super alloy Inconel 718 substrates were coated by using Atmosphere Plasma Spray (APS) system with three different (varying power) plasma spray parameters. All the sides of the 25mm x 10mm x 5mm thick substrates were completely covered with the bond coat and ceramic coating. FGM configuration was spray coated only on one side of the Inconel flat plates. Thermal shock cycle tests were performed on the coated specimen by following the ASTM B214-07 guidelines which comprised of introducing the coated specimen in a muffle furnace at 1150ºC, held in it for 2 minutes before removing from furnace followed by forced fan air cooling (one shock cycle). The specimen were periodically subjected to visual inspection for faults, before continuing the shock cycles, until the coating flaked off or cracked or detached from substrate. Cross section metallographic samples were prepared and analysed under SEM (Scanning Electron Microscope) and Energy Dispersive spectroscope (EDS) to study the as-sprayed coating morphology and interface quality, measure coating thickness, study defects characteristics and the chemical composition. Crystal structural phases were analysed using X-Ray Diffraction (XRD).

Keywords: Thermal barrier coatings; Zirconia based pyrochlore; Thermal shock cycles

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1. Introduction

Thermal Barrier Coatings (TBCs) have found extensive use in aerospace applications since the fifties: however research work continues with specific goals to find newer and innovative improved materials for various applications, configurations, characterization methods etc. The main purpose of TBCs is to reduce the surface temperatures of metal components on which they are applied and which are subjected to high temperature (1000˚C and above depending upon application) in service[1]. This is required to improve the life of the underlying metal components by providing protection from the harshness of the high temperature environment including oxidation, corrosion, erosion etc. and prevent failure. Inconel 718 is widely used as the metal in fabrication of aerospace components[2]. To increase the in-service performance temperature of this metal, thermal insulating material (in the form of coatings) having very low thermal conductivity and associated characteristics are required.

Currently, the most commonly used TBC material is 7-8 weight percent of Yttria Stabilized Zirconia (YSZ) which has found wide application in aerospace components (gas turbines) as the standard top coat TBC material (protective over layer)[3]. This is due to its ability to withstand temperatures of upto 1200˚C without spallation in service: which involves thermal shock and other thermal stresses related damage. YSZ can successfully decrease the surface temperature of the substrate material to a more tolerable range which is attributable to its thermal barrier effect due to low thermal conductivity properties[4,5]. However, due to the continuous thermal cyclic stresses generated during service the TBC system undergoes failure. One of the key reasons for this is the coefficient of thermal expansion (CTE) mismatch at higher temperatures (1000-1200˚C).

YSZ, a stable form of tetragonal-ZrO_2 or cubic-ZrO_2 undergoes destabilization to (m) monoclinic-ZrO_2 when subjected to >1200ºC associated with 3–5% volume expansion upon cooling. Due to the expansion characteristics, the specimen tends to fail or spall. Furthermore, the YSZ layers are also likely to sinter at T > 1200ºC, which increases the thermal conductivity of the ceramic topcoat (TC)[6]. Thermal stress and strain tolerance can be reduced through sintering and densification of the TC which significantly reduce the coating's durability in service.

To circumvent this issue, the concept of functionally graded materials (FGMs) has been explored. FGM materials are a mixture of the bond coat (BC) and ceramic top coat (TC) in varying ratios: which as intermediate coatings play important role of a middle layer that minimizes the CTE mismatch at elevated temperatures[7]. This helps to reduce the thermal expansion mismatch as the FGM layer is assumed to have thermal properties in between the two layers (bond and ceramic top coat). To further increase the operating temperatures of turbine engines, alternate TBC materials with low thermal coefficient, higher thermal stability and superior sintering resistance are required[8].

Improved TBC characteristics in zirconia based TBC material are also likely to be achieved by using novel materials. Pyrochlore of general composition, $A_2B_2O_7$ are used to develop TBCs with properties superior to YSZ[9]. Low-Thermal-Conductivity Rare-Earth Zirconate Pyrochlore - type system ($Re_2Zr_2O_7$, Re = rare earths such as La, Sm, Ce, Dy, Gd, etc.) have good potential for TBCs applications. In addition to low thermal coefficient and in contrast to the phase transformation the currently popular YSZ-TBCs undergoes at ~1200^0C, the RE Zirconate Pyrochlore TBCs exhibit very good phase stability at these and higher temperatures[10]. For applications involving TBCs, the goal is to develop Rare-Earth Zirconate Pyrochlore based coatings which promise improved high temperature properties (>1200ºC). These TBCs are expected to allow increased gas turbine efficiencies that will function effectively at higher than the current operating temperatures[11]. However, adhesion of the pyrochlore coatings to the bond coated substrates has been reported to be a cause for concern. FGM configurations may offer a solution to overcome the issue.

The present work comprises of using commercial YSZ in conventional and FGM configurations and laboratory synthesized plasma spray powders of Lanthanum Zirconate (LZ) by the solid-state method to prepare the pyrochlore coatings for comparison. NiCrAlY bond coat (BC) was used in all configurations. Thermal fatigue assessments were performed to study the potential to derive the benefits of FGM TBCs configuration (FGM: 50BC50TC) and Pyrochlore Zirconates TBCs over conventional TBCs system. FGM, and Pyrochlore Zirconates TBCs, 200-300µm thick on bond coated and YSZ coated on all surface of the substrates with three different (varying power) parameters, (P1, P2 and P3) prepared from the plasma spray powders were characterized for thermal shock tests in the muffle furnace at 1150ºC[12]. Scanning Electron Microscope (SEM) associated with Energy Dispersive X-Ray spectroscopy (EDS) was employed to study the powder morphology (result not given) as well as the coating and substrate-coating interface and

microstructure. The results and discussion pertaining to the TBC configuration, thermal fatigue and shock tests are reported. X-ray Diffractometer (XRD) was used to study the structural phases.

2. Experimental method and Materials

2.1. Powder Preparation

Commercially available raw powders of La_2O_3 (99%, Aldrich) and ZrO_2 (99%, Aldrich) were used for synthesising the plasma spray powder composition by the solid-state method. The process began with the wet mixing of the base powders in right proportions and is shown in Fig. 1. The powder underwent calcination process at 1150ºC in a high temperature furnace and the same powder was further calcined at 1500ºC with 6 hours soaking inside the furnace. The calcined powders were wet ball milled for 8 hours and were oven dried for 24 hours. Further the powders were sieved manually in order to get the plasma spray powder using the standard test method (ASTM B214-07). The process of sieving involved mixing the powder with 10% Poly vinyl alcohol (PVA) and passed through 25 mesh and transferred through 150 and 300 mesh sieves. The desired grain size for plasma spraying powder is in the range of (+ 53 to -106) micron which was achieved via sieving.

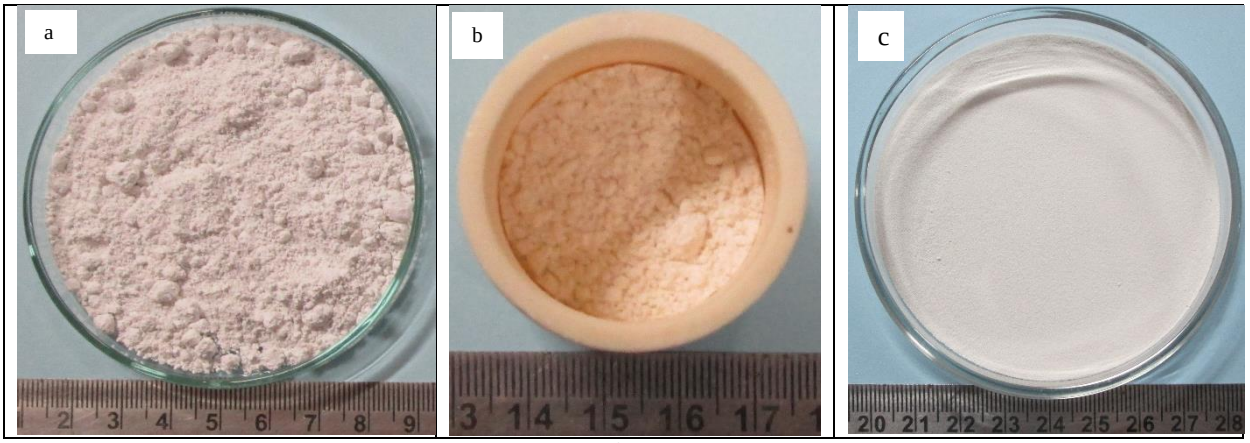

Fig. 1. (a) Raw mix (La_2O_3+ ZrO_2)- LZ; (b) LZ Powder after calcination at 1500ºC (c) LZ Plasma Sprayable Powder

2.2 Plasma Spray Coating

Commercially available NiCrAlY bond coat (AMDRY 956), 8% Y_2O_3 stabilized ZrO_2 (8YPSZ) top coat (TC) (METCO 204NS) and laboratory prepared plasma spray powder Lanthanum Zirconate (LZ TC) were used as starting powders to synthesise plasma spray coatings. Inconel 718 (a) bars of 25 mm x 10 mm x 5 mm (thickness) and (b) plate of 80 mm x 80 mm x 5 mm (thickness) were used as substrates to be coated by using an Atmospheric Plasma Spray (APS) system. Three different (varying power by varying the current and voltage) plasma spray parameters (P1, P2 and P3) were used in order to obtain the most suitable plasma spray parameter for coating the lab synthesized LZ on the substrate. The suitability was determined based on the parameter best suited for the coating to withstand the tests carried out at the high temperatures. Spray parameters are shown in Table 1.

Table 1. Plasma Spray Coating Parameters

Plasma Spray Parameters (P)	**NiCrAlY (Bond Coat)**	**P1 (YSZ/LZ)**	**P2 (YSZ/LZ)**	**P3 (YSZ/LZ)**
Voltage (V)	60	60	60	60
Current (A)	400	350	450	400
Power (kW)	24	21	27	24
Primary gas, Ar (SLPM)	57	37	35	14
Secondary gas, H_2 (SLPM)	17	8	4	5
Power feed rate (g/min)	45	15	34	10
Spray distance (mm)	100	100	100	100

2.3 Thermal Fatigue Studies:

In thermal fatigue evaluation, the six specimen that were coated on all surfaces by using three different plasma sprayed parameters (P1, P2 and P3) and one specimen (FGM) that was coated on one side surface underwent thermal fatigue cycle tests 1150ºC as shown in figure 2 (a and b).

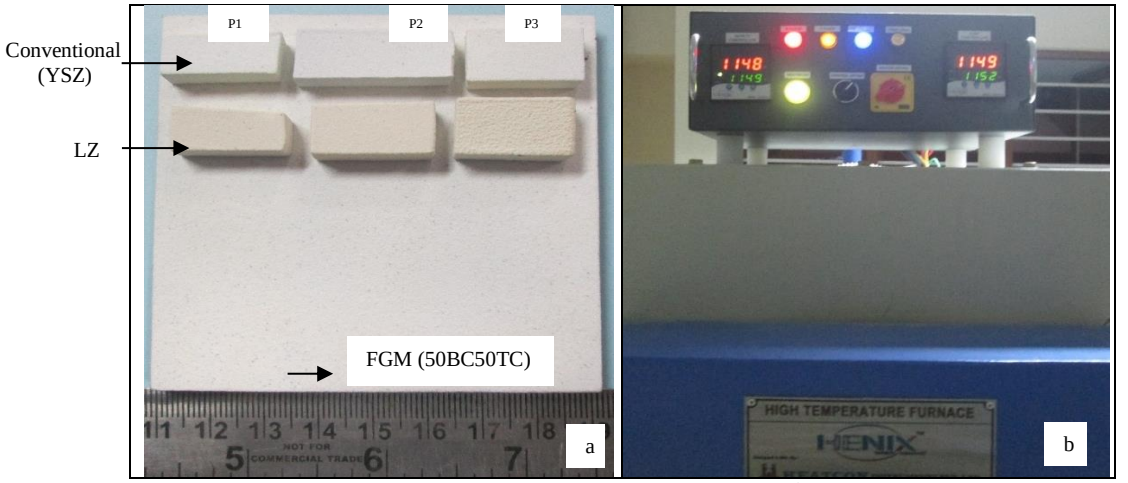

Fig.2. (a) As sprayed coated samples; (b) Temperature setting for thermal shock test;

The test comprised of placing the specimen inside the muffle furnace, maintained @ 1150ºC, hold for 2 minutes @ 1150ºC before air quenching (fan cooling) in laboratory ambient (Room temperature @~25ºC). The end of a 2-minute cool cycle completed one thermal shock cycle as shown in figure 3 (a and b). The tests were carried out based on the guidelines of the standard ASTM C 1171-16 and the goal was to determine which of the coated composition could withstand the most number of cycles without cracking or peeling away of the ceramic coatings. The coated samples (conventional, FGM 50BC50TC and LZ) were introduced in the high temperature furnace 1150º. After a certain number of cycles were completed, the specimen was taken off the furnace muffle, subjected to visual inspection for failure/detachment of coating and reintroduced into furnace. The cycles were repeated till coatings failed.

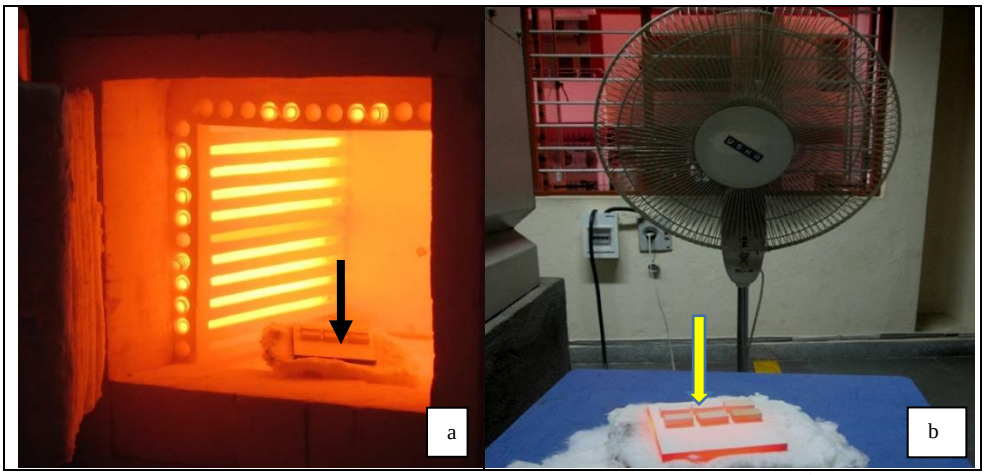

Fig.3. (a) Samples (shown with black arrow) were placed in the high temperature furnace;
(b) Air quenching using fan (yellow arrow shows hot samples removed from the furnace)

2.4 Material Characterization

Analyses of the crystallographic structural phases of the raw and plasma spray powders were carried out by using (XRD). Cross-section metallographic sections of as-sprayed coated specimen of thermal shock tested specimen were also analysed using SEM. The chemical composition of the LZ powders were analysed using EDS.

3. Results and Discussion

3.1 SEM (EDS) and XRD analysis of LZ

SEM and EDS were used to analyse the chemical composition on selected surface of LZ coated specimen shown in Fig. 4. Lanthanum (La), Zirconium (Zr) and oxygen (O) were found to be present, confirming the most likely composition to be Lanthanum Zirconate. XRD analysis confirmed the structural phase. XRD patterns of raw mix (La_2O_3+ ZrO_2), LZ calcined powder (1150ºC and 1500ºC) are shown in Figure 5 (a to c).

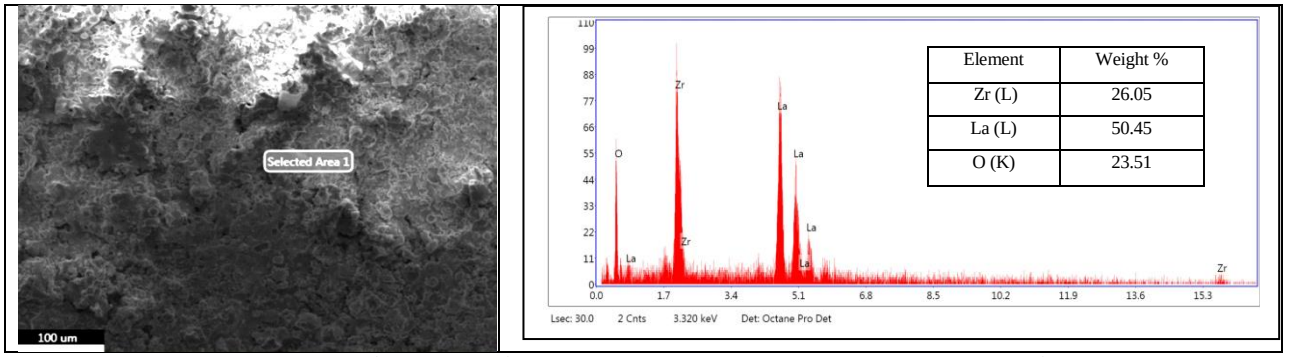

Fig. 4. EDS pattern of LZ coated surface showing Elemental composition and the spray- coated surface

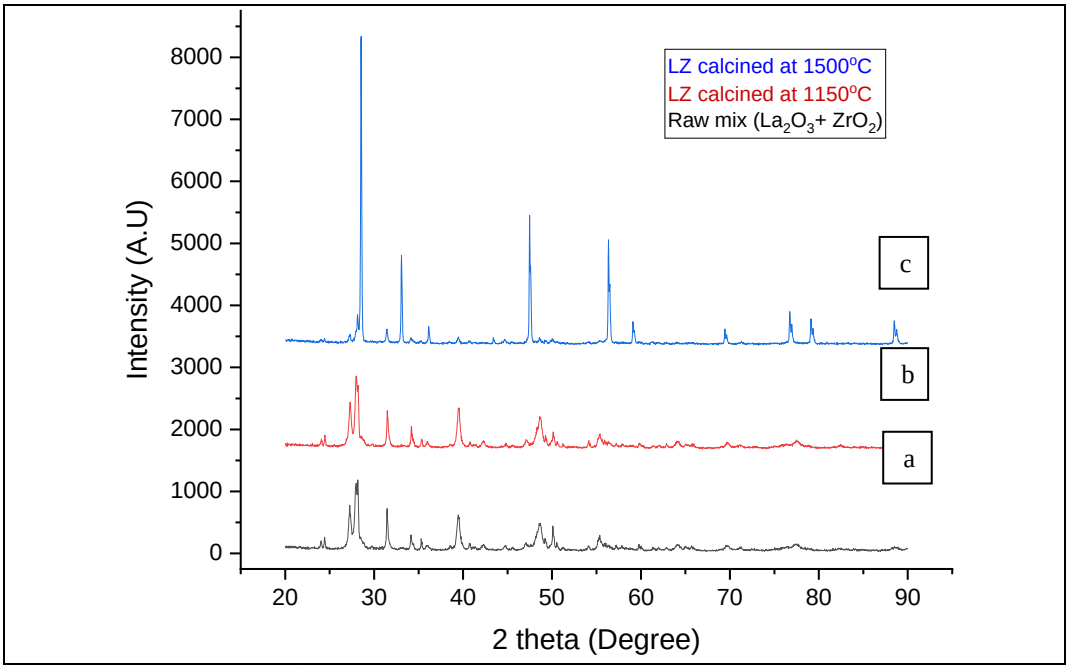

Fig. 5. XRD patterns of (a) raw mix (La_2O_3+ ZrO_2) ; (b) LZ calcined at 1150ºC; (c) LZ calcined at 1500ºC

XRD patterns shown in Fig. 5a, as expected showed the peaks pertaining to La_2O_3 and m-ZrO_2, the raw mix powder compositions. To obtain the compound, i.e. LZ, the raw mix powders were calcined at two temperatures i.e.1150 and 1500º C and the patterns are shown in Fig. 5 (b, c). While the initiation of compound formation was depicted by the XRD pattern for the mix calcined at 1500º C, complete Lanthanum Zirconate (LZ) phase was formed when the calcination temperature was 1500ºC. Peaks pertaining to neither La_2O_3 nor m-ZrO_2 phase was present in Figure 5c, indicating that phase formation of LZ was complete.

3.2 SEM Analysis Results of As-sprayed coating

Figures 6 (a to c) show the Scanning Electron Microscope (SEM) micrographs of cross section of as-sprayed specimen of (a) conventional, (b) FGM 50BC50TC and (c) LZ TBCs.

Fig 6 (a) shows the SEM morphology cross section of as-sprayed coated of the conventional specimen where BC and top coat (YSZ) is observed as two layer TBCs systems. Similar features were observed in LZ specimen as well (Fig.6b). In both TBCs system bond coat layer of 75 microns was sprayed on the Inconel 718 (NiCrAlY) and ceramic coating (TC) 300 microns was sprayed on over as the top coat. The interface between BC and TC in both the systems was smooth without defects, although with some porosity or grains pull out during polishing (metallographic cross section preparation). Whereas in FGM configurations a blend layer (wt. %(50BC+50TC)) was sprayed in between the bond coat and top coat (YSZ) of 100 microns thickness. Fig. 6c shows the micrograph depicting all the three layers (bond coat, bond coat-top coat blend and top coat).

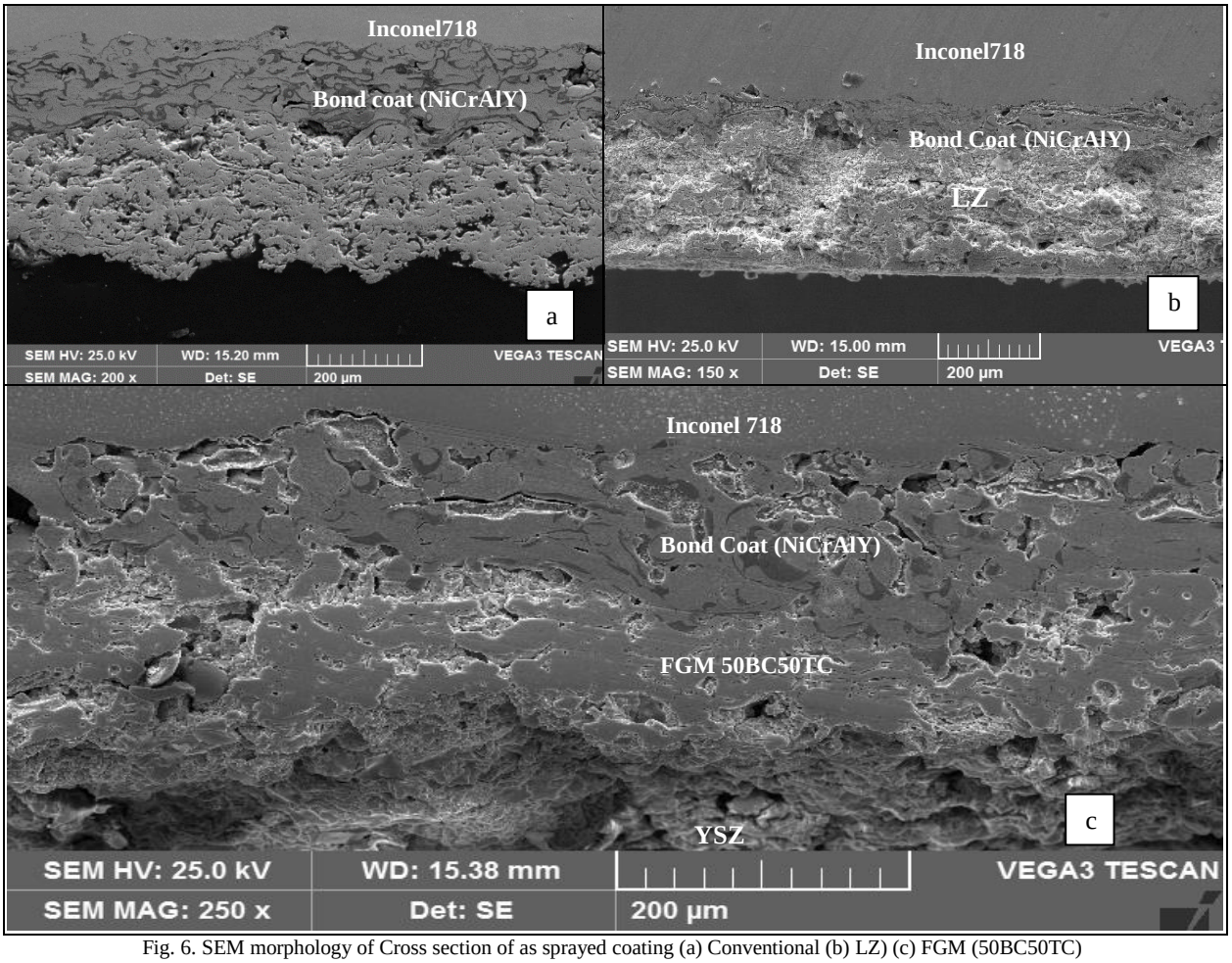

Fig. 6. SEM morphology of Cross section of as sprayed coating (a) Conventional (b) LZ) (c) FGM (50BC50TC)

3.3 Thermal shock cycle test results

Outcomes of thermal fatigue evaluation of specimen that underwent the assessment with different parameters of processing (P1, P2 and P3) under conventional, multi-layered FGM and LZ TBCs are shown in table 2.

Table 2. Thermal Shock cycle Test results

Parameters	No of thermal fatigue cycles @1150ºC & state of coated specimen			Remarks
	Conventional, YSZ	FGM 50BC50TC (Plate)	LZ	
P1 -21kW	100 (Not failed)	100 (Not Failed)	15 (Failed)	Conventional YSZ and FGM superior to LZ
P2 -27kW	100 (Not Failed)	Specimen not prepared	7 (Failed)	Conventional YSZ superior to LZ, FGM not evaluated
P3 -24kW	100 (Not Failed)	Specimen not prepared	30 (failed)	Conventional YSZ superior to LZ, although LZ sprayed using parameter P3 was found to be superior to those sprayed using parameters P1 and P2.

The findings shown in Table 2 are explained as the following. Conventional (commercial YSZ plasma spray powder) plasma spray coated in all the three parameters condition (P1, P2 and P3) yielded satisfactory results by withstanding at least 100 (test stopped at this stage) thermal shock cycles between 1150ºC and the ambient. This composition exhibited good stability (defect free specimen, no cracks, no peeling off the coating) when used at the high temperature. Figure 7 shows the three YSZ specimens at the end of 100 thermal shock cycles.

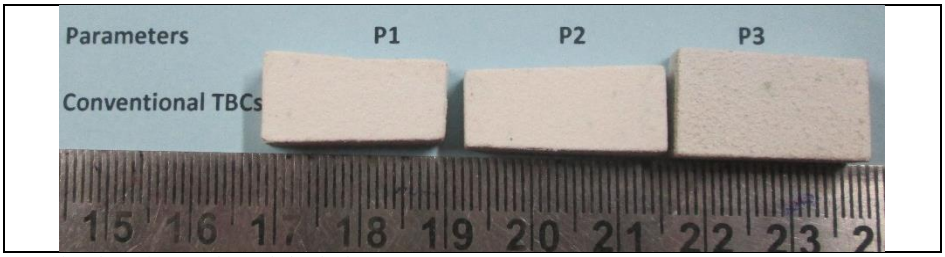

Fig.7. Conventional specimens' thermal shocked at 1150º C: Coatings with P1, P2 and P3 withstood 100 cycles without failure

Similar result was exhibited (or better results likely) by the coating in FGM configuration (spray parameter P1) that withstood up to 100 thermal shock cycles without failure: same as that of YSZ. The test was stopped at this stage before continuation to failure. It is important to note that the coating in this configuration comprised of only thickness build up on one side of the plate (other samples were coated on all six side) to the specifications of top coat parameter (P1 - P3). In spite of this constraint the specimen performed very well. Figure 8 shows the FGM plate specimen at the conclusion of 100 thermal fatigue cycles. Further tests are in progress in the laboratory.

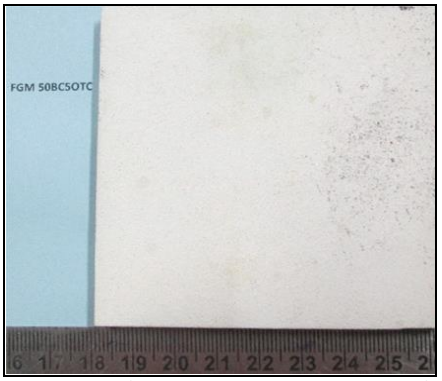

Fig.8. FGM 50BC50TC after 100 thermal shock cycles (not failed) at 1150º C

When subjected to same tests, LZ composition did not live up to the expectations and none of the specimen fabricated under the three spray parameters (P1, P2 and P3) withstood more than 30 shock cycles. Figure 9 shows the LZ specimen at the end of 7 – 30 thermal shock cycles. Specimen fabricated in parameter P1 failed in as early as 7 shock cycles, sprayed in parameter P2 failed in 15 cycles and that sprayed in parameter P3 failed in 30 cycles. However, one favourable aspect that has emerged out of this exercise is that LZ composition when spray coated under P3 spray condition, withstood 30 cycles and establishes of the superiority of the LZ coating when spray coated by following the parameter P3 only among the three parameters studied in this work.

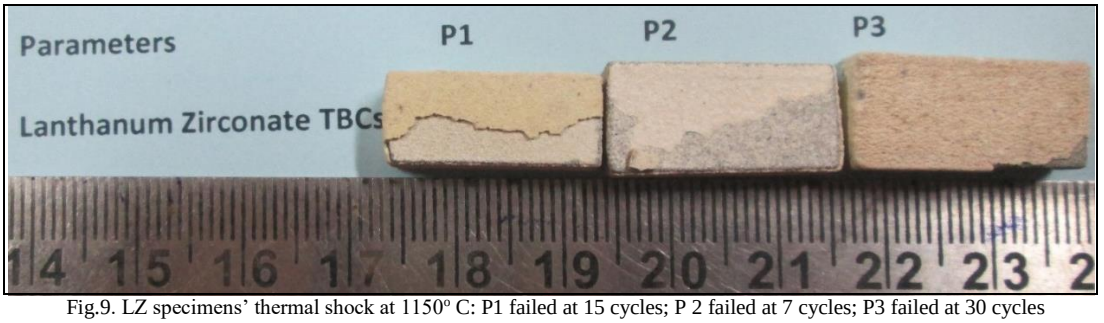

Fig.9. LZ specimens' thermal shock at 1150º C: P1 failed at 15 cycles; P 2 failed at 7 cycles; P3 failed at 30 cycles

To summarize the results, conventional YSZ and FGM 50BC50TC specimens withstood at least 100 cycles without any degradation / failure while the best of LZ specimen withstood only 30 cycles.

The damage mechanism of the LZ coating is most likely due to disparity in thermal expansion characteristics between the substrate and TBC [13]. Further experiments are warranted to arrive at the optimum spray conditions to synthesise LZ coatings, which are known to possess thermal conductivity values lower than that of YSZ and therefore will perform as superior TBCs. Further work is in progress in this direction. One more possibility being tried out in order to circumvent this problem is incorporation of YSZ layer deposited between the bond coat and top coat (LZ) to form multi-layered coating configuration or in FGM configuration. This is expected to integrate the benefits of favourable thermal shock resistance of YSZ coating in FGM configuration and lower thermal conductivity of LZ. Thus the expansion coefficient mismatch between the TBC and the base metal plate is expected to be greatly reduced. [14].

4. Conclusions

1. Conventional, Functional Graded Materials (blended configuration) and Lanthanum Zirconate thermal barrier coatings (TBCs) were prepared by plasma spray coating the spray powders.
2. Lanthanum Zirconate composition and plasma spray powders were synthesized in the laboratory. Single phase formation of the compound Lanthanum Zirconate (LZ) was confirmed via x-ray diffractometry when the powders were calcined at 1500ºC.
3. The coatings were plasma sprayed by varying the spray parameters to determine the optimum coating condition especially for lab synthesized LZ powder.
4. All the plasma spray coated specimen underwent thermal fatigue test cycles between 1150ºC and ambient in a muffle furnace by following ASTM guidelines.
5. FGM (50% bond coat + 50% top coat as intermediary layer) showed significant advantage in terms of coating life at 1150ºC over conventional specimen
6. Lanthanum Zirconate (LZ) coatings did not perform as well as YSZ or FGM coatings. The damage mechanism of LZ coatings was attributable most likely to of the LZ due to expansion coefficient mismatch between TBCs and underlying metal plates.
7. The coatings in FGM formation exhibited superior thermal shock cycle resistance which may possibly be attributable to improved adhesion and increased adhesion (inter layer) strength in the FGM configuration.
8. Among the three plasma spray parameters experimented with, one parameter was found to be slightly more suited

to spray coat the Lanthanum Zirconate. This conclusion was based on the thermal shock test results for the LZ, plasma spray coated on three different plasma power settings.

9. LZ in combination with YSZ and intermediary layer or in FGM configuration with NiCrAlY bond coat configuration is expected to perform in a superior manner than what was exhibited in the present framework of experiments.

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Performance and Steady State Heat Transfer Analysis of Functionally Graded Thermal Barrier Coatings Systems

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Abstract

Thermal barrier coatings (TBC's), typically 8 wt.% Yttria Stabilized Zirconia (8YSZ), in single layered configuration have been traditionally used in aerospace components to protect them from degradation at high temperatures and to improve the thermal efficiency of the system. This paper compares the performance of two types of TBC configurations: single layered and multilayered functionally graded materials (FGM). Aerospace alloy, Inconel 718 substrates, NiCrAlY bond coat (BC) and 8YPSZ top coat (TC) were the materials used. FGM configuration was used to improve the durability and life of the conventional TBC system by reducing the coefficient of thermal expansion (CTE) mismatch. The TBCs were subjected to thermal fatigue (thermal shock and thermal barrier test) in laboratory scale burner rig test and oxidation stability test in high temperature furnace upto 1000℃. The as-sprayed and thermal fatigue tested specimen were characterized by X-ray diffraction (XRD) analysis and Scanning Electron Microscope (micro-structure). Results are discussed in the light of suitability of coating configuration, thermal fatigue and spalling characteristics with reference to aerospace applications at temperatures in the 900^0C to 1500^0C range. Computational work was carried out comprising a simulation model involving the developed TBCs.

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Keywords: Funtionally Graded Materials; Thermal Barrier Coatings; High Temperature Performance; FEM Analysis; SEM analysis

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1. Introduction

Thermal barrier coatings (TBCs) provide thermal resistance to the metals they are applied on and reduce the substrate surface temperature of the metallic components in many power generation systems such as diesel engines, gas turbines and aircraft engines [1]. They contribute to achieve improved performance, efficiency and increase the service life of the components [2]. The major contribution to the application range of TBC system used in aircraft engines consist of a 100 micrometer to 2mm thick thermally insulated ceramic layer and 50-120 μm metallic bond coat layer between the ceramic layer and surface of metal components, which are commonly referred to as duplex TBCs. Plasma sprayed Yttrium oxide (8% Y_2O_3) stabilized zirconia (ZrO_2) thermal barrier coatings (TBCs) with MCrAlY (M is a metal which can be Ni, Co or a combination of Ni and Co) bond coat is a well-established TBC system [3]. Yttria stabilized zirconia (YSZ) possesses low thermal conductivity, low coefficient of thermal expansion, suitable microstructure, thermal fatigue resistance, sintering and oxidation resistance and useful in service upto 1150^0C [4]. Being a critical component, the gas turbine engines are always coated by Electron beam physical vapor deposition (EBPVD) technique, although atmospheric plasma spraying (APS) is the next best and cost-effective alternative for research purposes.

APS is a well-researched and conventional method to fabricate TBC's [5]. NiCrAlY is often used as bond coats and YSZ ceramic is then deposited as the top coat. Stabilizers like Yttrium oxide (yttria) maintain the desired tetragonal ZrO_2 phase at high temperature (<1200^0C) and at rapid quenching rates. But the main problem leading to the failure of the TBC system is the coefficient of thermal expansion mismatch (CTE) at high temperatures between the ceramic top coat and the metallic bond coat [6]. The CTE mismatch between the metallic substrate, bond coat and the ceramic contribute to buildup of stresses at the interfaces, leading to adhesive failure and sometime within inter-ceramic layers leading to cohesive failure.

1.1 Limitation of Yttria Stabilized Zirconia: resolution via Functionally Graded Materials

Zirconia partially stabilized with 7~8 wt. % yttria (YSZ) is the current state of-the-art thermal barrier coating material and its thermal conductivity (k) is ~2.12 W/m-K at 800℃ [7]. At T >1200℃, YSZ transforms from tetragonal ZrO_2 phase to a mixture of tetragonal and cubic phase (t and c-ZrO_2 phases, respectively) which leads to destabilizing the YSZ structure and during cooling process t-zirconia phase returns to m-zirconia phase with a volume expansion of about 3–5 vol.%, resulting in the spallation of TBCs. Furthermore, YSZ is prone to sintering, where k gradually increases and makes them less effective. Thermal stress and strain tolerance are reduced due to sintered and densified coatings further reducing the coatings durability and adhesion strength [7].

The method used in this study to improve the characteristics of YSZ TBCs is by introducing a layer of functionally graded material (FGM), a concept that makes use of compositional variations to improve the life and durability of the conventional TBC system. TBCs significantly reduce the temperature that these metallic components experience and therefore increase their thermal shock/fatigue life and protect them from oxidation. Further benefits are expected by usage of functionally graded materials TBCs [8][9]. Use of FGM based TBCs recommend an excellent avenue to enhance the resistance of the TBCs to delamination. The outermost layer (top coat) on the surface in FGM systems are ceramic rich (conventional ceramic layer) to provide thermal insulation [10]: whereas the FGM coating is used as an intermediate layer below the top coat in the conventional 'duplex' architecture i.e. it is used in between the Top coat (TC) and Bond Coat (BC). The FGM layer has properties in between the ceramic top coat and metallic bond coat, so that there is no sudden change in coating characteristics but gradual transition, thereby improving the stability of the system.

In the present work, FGM systems of NiCrAlY (BC) and 8YSZ (TC) were obtained by mixing the two plasma sprayable powders and passing them through the plasma in an APS system. FGM coatings can also be obtained by using multiple powder feed inlets in torch where, in one the ceramic TC powder flows while in the other the metallic BC powder. However, it is not easy to control the spray parameters to form uniform coating layers as the two kinds of starting powders have different densities, particle sizes, morphologies, melting points and flowability. This paper presents the results obtained from FGM-TBC coatings, synthesized by physically mixing (blending) the NiCrAlY & 8YPSZ plasma sprayable powders in predefined percentages (weight ratios).

2. Experimental Procedures

2.1 Materials and Methodology

The metal substrates used in this work were Nickel based super alloy (Inconel 718) of dimensions 80 mm X 80 mm and thickness of 5 mm with composition (Ni-54.75%, Cr-17.95%, Nb+Ta-5.18%, Mo-2.98%). 50 mm X 10 mm X 5 mm thick substrates were used for oxidation stability tests. Prior to deposition on the metal substrate, the specimens were grit blasted with alumina followed by plasma spray coating in FGM configurations. Bond coat (BC)- AMDRY 962 (Ni-22Cr-10Al-1Y, -106 +52 µm) and Top coat (TC)- METCO 204NS (8% Y_2O_3-ZrO_2, -106+11 µm) plasma sprayable powders were used. The coatings on substrate were prepared by using robot controlled 100 KW Metco Sulzer Air Plasma Spray facility. Ceramic Coatings in two configurations were prepared: (a) conventional TBC's which comprised of a bond coat (~ 50-micron thick) layer and top coat layer (~ 250-micron thick TC layer) on the substrate (b) FGM consisting of three layers over the substrate (bond coat, (bond coat –top coat blend) and finally the top coat overlay). Prior to deposition on the metal substrate, the specimens were grit blasted with alumina followed by plasma spray coating in conventional and FGM configurations. The FGM'S configurations were (a) BC-(25BC+75TC) blend-TC (b) BC-(50BC+50TC) blend-TC and (c) BC-(60BC+40TC) blend-TC. Spray parameters that were used during the spraying of the bond coat and top coat are shown in Table.1.

Table 1: Spray parameters used for bond coat and top coat application

Parameter	NiCrAlY (Bond Coat)	%8YSZ (Top Coat)
Voltage (V)	75	70
Current (A)	400	550
Primary gas, Ar (1/min)	57	38
Secondary gas, H_2(1/min)	17	17
Power feed rate (g/min)	45	35
Spray distance (mm)	10	10

Figure 1 shows the schematic of the conventional and FGM (typical) configuration in cross section

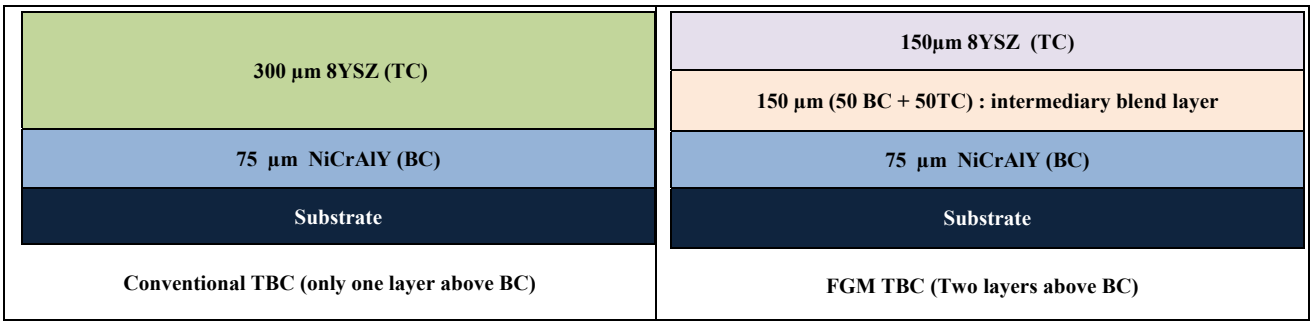

300 µm 8YSZ (TC)
75 µm NiCrAlY (BC)
Substrate
Conventional TBC (only one layer above BC)
150µm 8YSZ (TC)
150 µm (50 BC + 50TC) : intermediary blend layer
75 µm NiCrAlY (BC)
Substrate
FGM TBC (Two layers above BC)

Fig 1. Typical TBC configurations (Conventional and FGM)

2.2 Thermal Shock (Fatigue) Tests:

Thermal Shock resistance is a very important factor deciding the life of the thermal barrier coating (TBC). In order to measure the thermal shock resistance of the coatings, the ceramic surface was heated to a predefined high temperature for 60 seconds (one minute) and the flame was removed, and ceramic surface was force cooled with air for 60 seconds (one minute). This completed one cycle which induces a thermal strain in the TBC system. The failure typically occurs due to the presence of residual thermo-mechanical stresses generated in the TBC system. These stresses are caused due to the difference in coefficient of thermal expansion (CTE) mismatch between the ceramic top coat (TC) and the metallic bond coat (BC) or in some cases between the BC and the substrate.

A non-contact Infra-red thermometer (gun) was used to measure the temperature on ceramic coating surface where oxyacetylene flame was focused (Fig.2a).

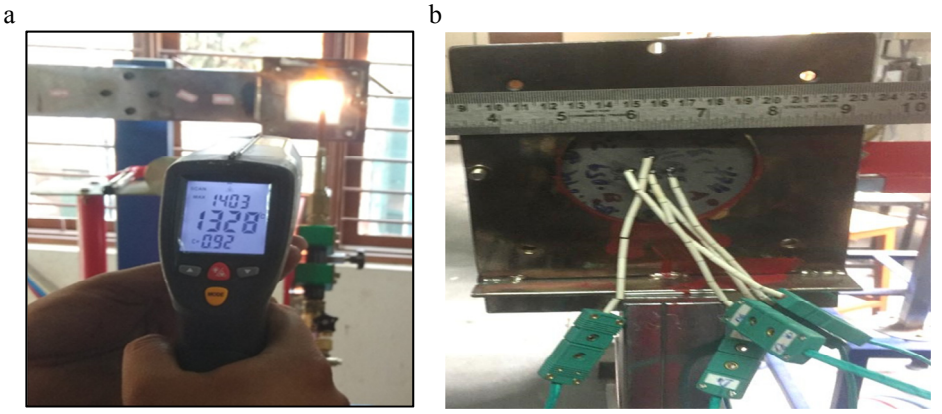


Fig. 2. (a) Thermal shock test (Flame focussed on ceramic coating, temperature measurement via non-contact IR thermometer); (b) Thermo-couples embedded at back of substrate to measure the metal temperature (flame focused on ceramic side)

2.3 Thermal Barrier Tests

Thermal barrier test is generally conducted as an indicative laboratory scale experiment, used by both, the academia and the industries to determine the thermal gradient provided by the insulating coating. This test can give a consistent approximation of the temperature drop across the coating. The test in this work involved subjecting the outer most coated surface of the 80 mm X 80 mm and 5 mm thick plate with a flame at desired temperature focused at the mid-portion of the coating by allowing the ceramic surface adequate time (about 1 hour) to attain the intended temperature under the steady flame conditions (flame temperatures (T) at 1000℃ and up to 1500℃, in increments of 100 degrees). Pt-PtRh thermocouples and non-contact IR thermometers were used to measure the temperatures on the substrate (back side) and ceramic temperatures (flame side) respectively. Five holes of different depths (4.7mm, 4.5mm, 4.3mm, 4.2mm and 4 mm) were drilled into the back of the substrates and PtPt-Rh thermocouples were embedded into the holes at those locations as shown in Fig. 2b. This method ensured good contact between the substrate and the thermocouple tip and accurate measurement of the substrate temperature during the thermal barrier test

2.4 Oxidation Stability Test:

Oxidation stability of the coated system plays a vital role to determine its thermo-mechanical behaviour and thus to estimate the life of the ceramic coat when subjected to high temperature environment [11] [12]. To study the isothermal cyclic oxidation behaviours and microstructure changes of conventional TBC and different FGM composition, completely coated (all sides covered with ceramic) Inconel 718 specimen of dimensions 50 mm X 10 mm X 5 mm substrates (conventional and FGM configurations) were used for oxidation stability tests at 800℃ and 1000℃. The tests were performed by introducing the samples in a furnace at room temperature, raising to a temperature up to 800℃ (or 1000℃), holding at the desired high temperature for 12 hours, followed by cooling inside the furnace for 12 hours to room temperature. The specimen was removed, visually inspected for defects, before repeating the cycle, until the coating showed signs of cracking or peeling off. Specimen used for oxidation stability tests are shown in figures later in this paper along with shock tested specimen.

2.5 Metrological Analysis (Microstructure and Structural phase)

Metallographic polished cross-sections were prepared of the oxidation tested specimen to investigate the coating-substrate interface characteristics, micro structure and analysed by using Scanning Electron Microscope (SEM). Structural Phase analysis of the coatings was carried out via X-ray diffractometry (XRD).

3. Finite Element Models and Analysis

Some of the obtained experimental results were compared via results obtained by Finite element values to validate the process. The model was prepared and meshed using Hypermesh 13.0. The steady state heat transfer analysis was carried out by using Ansys Fluent 16.

3.1 Design Parameters

The dimensions of the models are as follows; Substrate:80 mm x 80 mm x 5 mm; Bond Coat: 80 mm x 80 mm x 75μm; Top Coat: 80 mm x 80 mm x 300 μm. Table 2 shows specimen layer composition.

Table 2: Specimen layer composition.

Composition	Substrate	Bond Coat (BC)	Intermediate Coat	Top Coat (TC)
1	Inconel 718	NiCrAlY	None	8YPSZ
2	Inconel 718	NiCrAlY	50wt%BC+50wt%TC	8YPSZ

3.2 Material Properties

The properties of all the elements used in the model are shown in Table 3.

Table 3: Material Properties

Materials Properties	Inconel 718	NiCrAlY	50BC-50TC FGM	8YPSZ
Thermal Conductivity	27.81 W/mK	16 W/mK [13]	6.98W/mK	1.88 W/mK [13]
Density	8192 Kg/m^3	7710 Kg/m^3 [13]	6800Kg/m^3	6000 Kg/m^3 [13]
Specific Heat	550 J/kgK	520 J/kgK [13]	600J/kgK	520 J/kgK [13]

3.3 Mesh and Boundary Conditions

The meshing of the model was done with varying mesh sizes due to the use micron size coating. A 20mm diameter area was created on the surface of the top coat. This region was subjected to constant temperature of 1000℃. The region, apart from the 20mm area, along with the 4 sides and the bottom (uncoated region) was subjected to free convection at 27℃ and having a thermal convection coefficient of 10 W/m^2K.

4. Results and Discussion

4.1 Thermal Shock Test

The results pertain to the test when the hot face (ceramic surface) was subjected to the harsh environment (flame temperature at ceramic surface at 1200℃ and 1400℃). The conventional specimen when exposed to 1200℃ and 1400℃ (separate tests) failed at the end of 158 and 35 thermal shock cycles respectively as shown in Fig. 3(a, b), while the specimen with FGM configuration (c) BC-(50BC+50TC)-TC withstood more than 273 cycles without failure at 1200℃ and failed only at 184 cycles when exposed to 1400^{o}C. Failure was recorded when the topmost ceramic layer (visible to naked eye) either cracked or showed signs of delamination as shown in Fig. 3(a, b c and d).

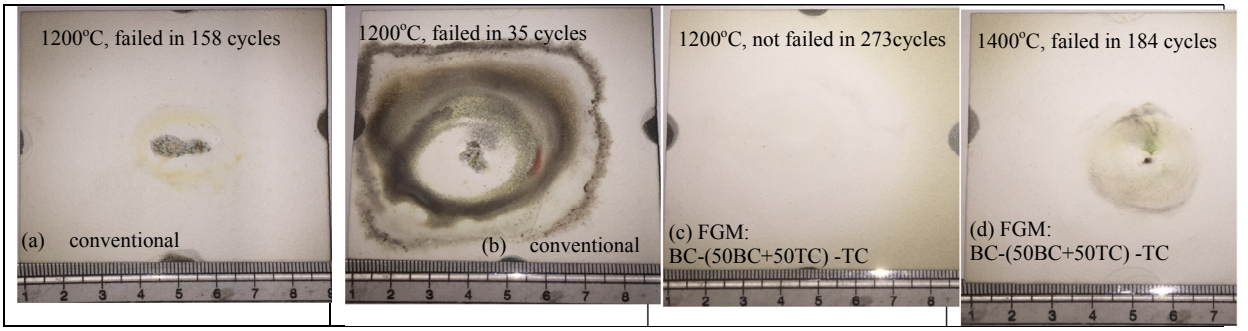


Fig. 3. (a thru d): Thermal shock tested specimen at 1200°C and 1400°C, Conventional and FGM (BC – (50BC+50TC) - TC)

Furthermore, the blended (FGM) configurations i.e. (BC- (25BC+75TC) – TC) and (BC-(60BC+40TC)-TC) also showed significant advantage in terms of life when shock cycled between 1200℃ and ambient. They withstood ~/> 200 shock cycles. In contrast, the (BC-(25BC+75TC)-TC) FGM configuration did not exhibit any improvement over the conventional when cycled between 1400℃ and ambient (withstood only 35 cycles, same as conventional) but the (BC-(60BC+40TC)-TC) FGM withstood more than 180 cycles before failure (like (BC-(50BC+50TC)-TC) FGM.

From the above results we may conclude that an introduction of FGM layer plays an important role in determining the life of coatings under the thermal shock cycles test conditions adopted in this work. The highly superior characteristics of the multilayered FGM configurations in TBCs are established.

4.2 Oxidation Test

The conventional (non-FGM) specimen failed in a span of 96 hours in oxidation stability test at 800℃, while no failure was observed among the FGM configuration even after 264 hours. Fig 4 shows the TBC specimens before and after oxidation stability test at 800℃ in conventional and FGM configurations.

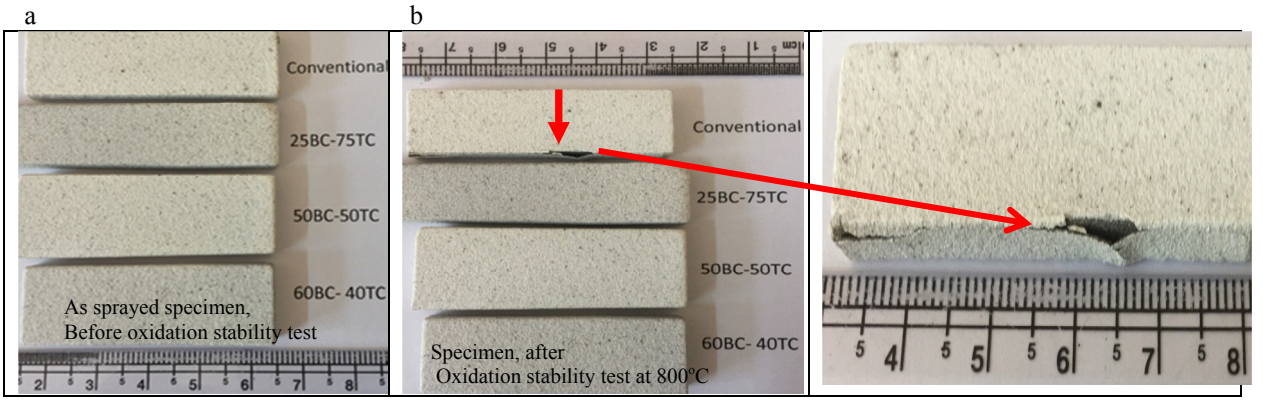


Fig. 4. TBC Specimen before and after oxidation stability tests at 800°C (Conventional and FGM configurations);(a) FGM configurations without any cracks on the surface after test; (b) Arrows show the cracks in conventionally coated specimen 800°C/96 hours: 24 hours anneal;

In a pattern similar to that exhibited by specimen that underwent thermal shock cycle test (Flame), the conventional specimen failed in span of 24 hours at 1000℃. Only the FGM with (BC- 50BC+50TC-TC) configuration withstood an oxidation test >60 hrs of oxidation stability test at 1000℃. From these experiments, while it is certain that FGM (NiCrAlY+8YPSZ blend as intermediate layers between bond coat and top coat) TBCs exhibit much superior performance compared to conventional 8YPSZ TBC, the exact mechanism attributable to the much superior

performance of FGM TBC with (BC- 50BC+50TC-TC) configuration is not clearly understood and detailed analysis is warranted to be performed. The specimen subjected to oxidation stability test at 1000^{O}C are shown in Fig. 5.

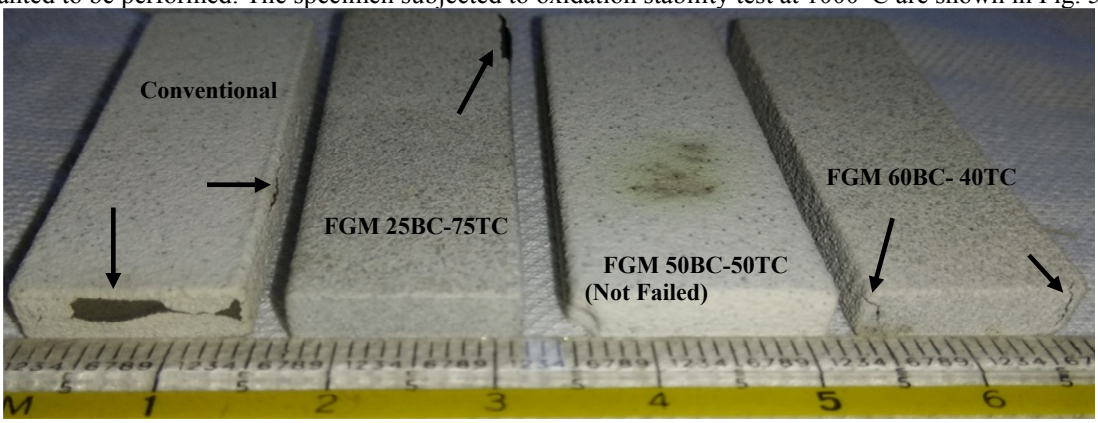
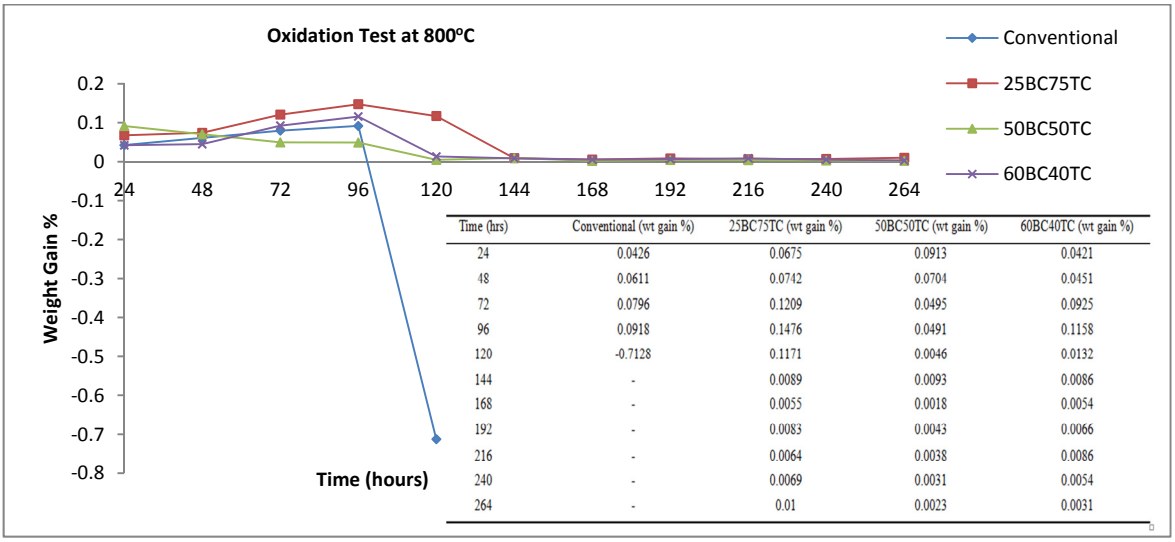


Fig. 5. Specimen after oxidation stability tests (conventional and FGM) at 1000^{O}C: (Arrows show the failure location)

Oxidation stability tests also include the study of weight gained by the specimen under study. The weight gain is attributed to the oxidation of the substrate material due to the oxygen ion transfer through the porous (upto 12% porosity) top coat ceramic materials (8YPSZ) at the test temperature. Once steady state is attained, no further weight gain is anticipated because the oxide layer protects the material from further weight gain. The percentage weight gain experienced by the specimen during oxidation stability test with temperature of furnace maintained at 800°C is shown in Fig 6. After 96 hours of exposure at 800^{0}C, the conventional specimen showed severe reduction in weight which is due to spallation (cracking and flaking off) of the coating.



Time (hrs)	Conventional (wt gain %)	25BC75TC (wt gain %)	50BC50TC (wt gain %)	60BC40TC (wt gain %)
24	0.0426	0.0675	0.0913	0.0421
48	0.0611	0.0742	0.0704	0.0451
72	0.0796	0.1209	0.0495	0.0925
96	0.0918	0.1476	0.0491	0.1158
120	-0.7128	0.1171	0.0046	0.0132
144	-	0.0089	0.0093	0.0086
168	-	0.0055	0.0018	0.0054
192	-	0.0083	0.0043	0.0066
216	-	0.0064	0.0038	0.0086
240	-	0.0069	0.0031	0.0054
264	-	0.01	0.0023	0.0031

Fig 6. Specimen after oxidation stability tests at 800ºC

The cracking and spallation of the ceramic top coat is associated with the internal stresses generated in the system at the interfaces, which originate from the thermal expansion mismatch and oxidation of the bond coat forming a thermally grown oxide (TGO) layer of Al_2O_3. The TGO layer is actually beneficial to an extent due to its low thermal conductivity values and therefore protects the substrate from further damage. However, once the TGO layer thickness exceeds a certain value (typically 5-7µm) then, the TBC system fails due to poor adhesion at the ceramic-bond coat interface. Yet again, the results demonstrate the major improvement exhibited by TBCs in the functionally

graded materials configurations (intermediate layers of 25BC+75TC, 50BC+50TC, 60BC+40TC) in terms of service life at high temperatures. This aspect is revealed by the absence of any defects or cracks on the ceramic surface of the specimen (Fig 5) and weight gain values (Fig. 6). The results of the weight gain study performed on similar specimen during oxidation stability tests at 1000^0C are shown in Fig 8. The trends shown by the specimen when tested at 800^0C was seen yet again, except for difference in the hours taken to failure/continue to survive the harsh tests. Details are not included in this paper.

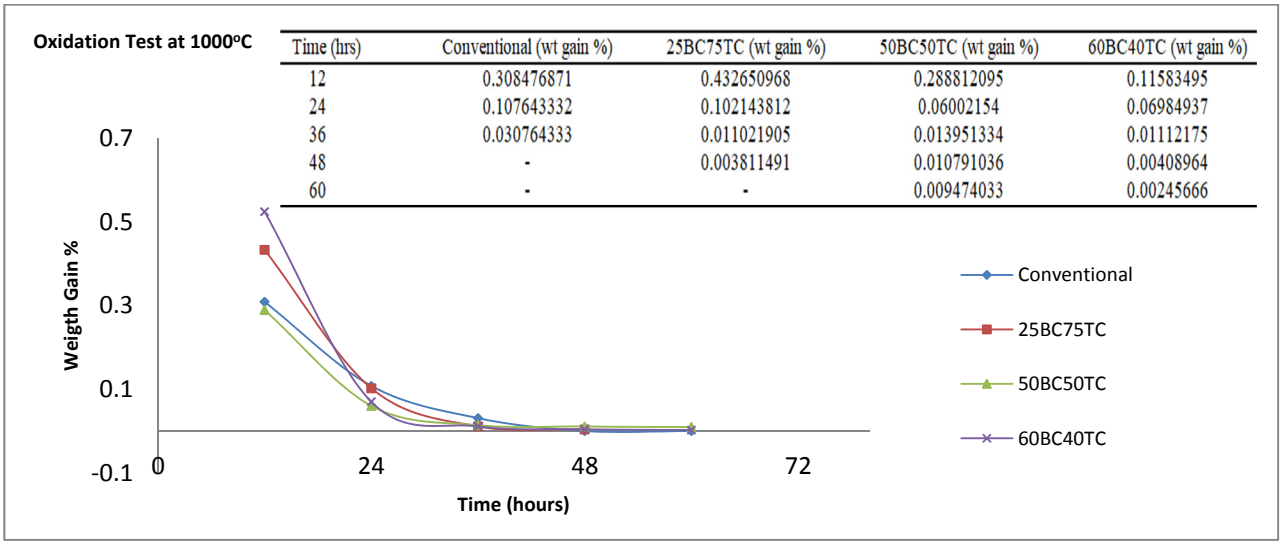


Fig. 7. Specimen after oxidation stability tests at 1000^oC

4.3 Microscopy (SEM) Results

Viewed in the SEM, the polished cross section metallographic specimen of the conventional TBC system, subjected to oxidation stability test at 800^0C, exhibits the spalled coating layer from the substrate (Fig 8). The main cause for the spallation has already been discussed in the previous section.

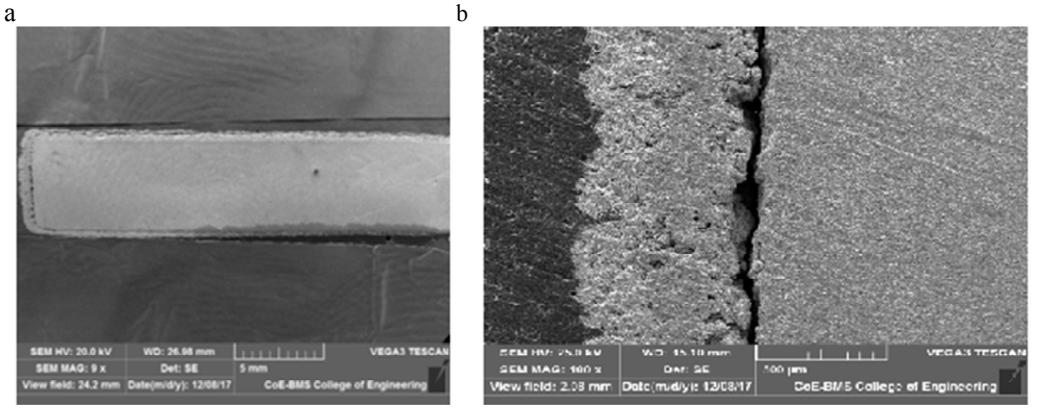


Fig. 8. SEM Micrographs of conventional coated specimen (metallographic cross section) after oxidation test at 800^OC
(a) Macro photograph (b) SEM results show spallation between TBC system and metallic substrate

Fig. 9 shows a typical FGM TBC system studied under identical test conditions which shows no sign of failure at the coating substrate or bond coat interface.

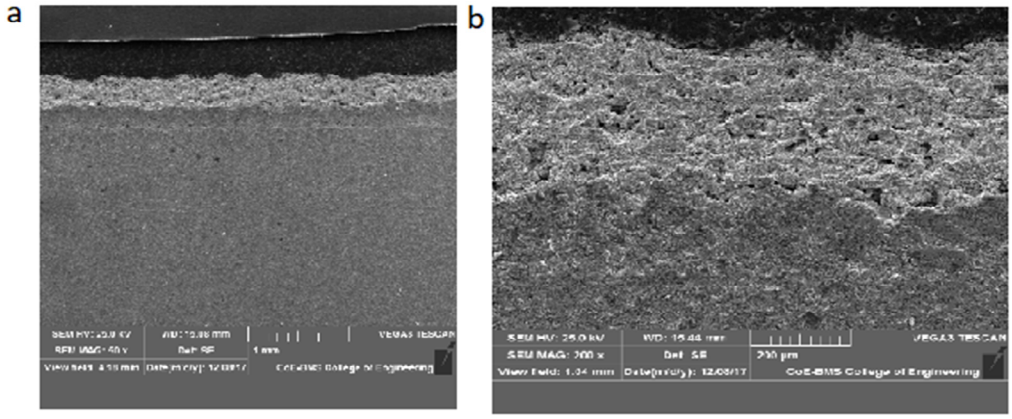


Fig. 9. SEM Micrographs of TBCs in FGM (50BC-50TC) configuration specimen after oxidation test 800^{O}C (metallographic cross section);

4.4 Thermal Barrier Test Results

The specimens (conventional and FGM (50BC+50TC) that were subjected to thermal barrier test did not show significant variation in temperature drop from each other. The temperature drop exhibited by the coating in conventional and FGM configuration varied between 30^{O}C and 60^{O}C. Marginal drop (as expected) in barrier effect was exhibited by the FGM configuration which may be attributed to small thickness of the top most coat (pure ceramic). The test results are shown in Fig.10.

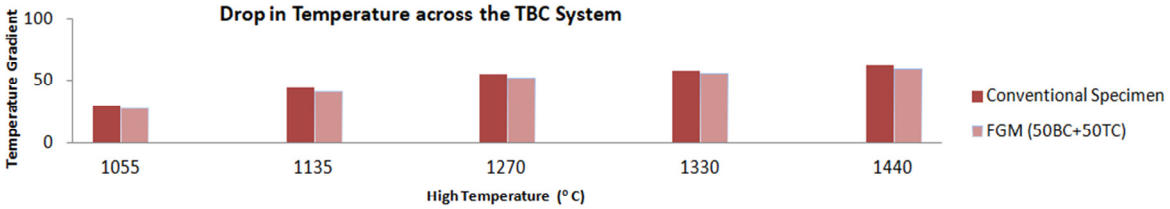


Fig. 10. Results of thermal barrier test (temperature gradient across coating)

4.5 Computational Analysis Results

Figure 11 (a through c) shows the temperature flow profile of the conventional and FGM (50BC+50TBC) TBC subjected to 1000^{0}C at the ceramic side and substrate (uncoated). While 11a depicts the high temperature face of the ceramic exposed to the flame, 11 (b &c) show the substrate (uncoated side).

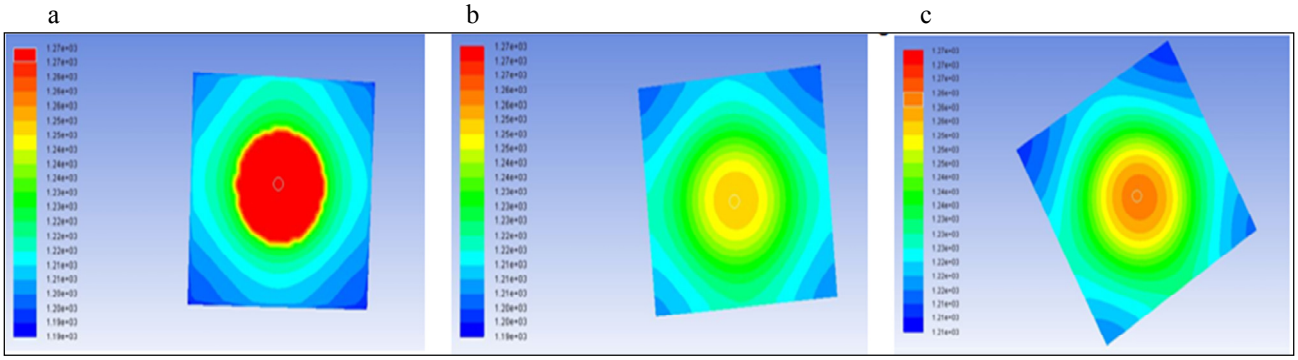


Fig. 11. Specimen subjected at 1000^{0}C (a) Ceramic Coated side (b) Substrate side (Conventional) (c) Substrate side of FGM (50BC+50TC)

The lower heat flow rate seen in Fig 11b pertains to the substrate in conventional configuration and the relatively higher heat flow rate to the substrate in FGM configuration. Comparing Fig. 11 (b) and (c), it is evident that the addition of an intermediate FGM layer alters the heat flow pattern. This is because, the FGM layer consists of a mixture of ceramic material having lower thermal conductivity (8YPSZ) and an alloy (NiCrAlY) having higher thermal conductivity. Due to this gap in k value, the overall k of the FGM layer is less than the metallic BC and greater than the ceramic TC. This results in higher heat flow rate in FGM configuration when compared to conventional. The drop at the centre (across the coating and substrate) in case of FGM was ~13^0C whereas the drop was ~16^0C for conventional TBC system. This may be because certain coating characteristic (i.e. porosity) has not been considered in the model presented here. The trend set by the two types of configurations in terms of temperature drop has been verified via experimentation (described in section 4.4)

5. Conclusion

8YPSZ and functionally graded coatings prepared from NiCrAlY bond coat and 8YPSZ blends as intermediary layers were studied for thermal fatigue characteristics. The conventional or duplex architecture of TBC with YSZ as top coat and NiCrAlY as bond coat performed fairly well up to temperatures of 1000^0C. As the temperature increased (<1200^0C) its performance gradually reduced over time which may be due to thermal expansion coefficient mismatch attributed to sudden change in coating characteristics (conventional) rather than gradual change offered by FGM. Further increase in service temperature leads to higher CTE mismatch at the interfaces thus, reducing service life of the TBC system. Use of FGM layer has improved performance in terms of thermal fatigue resistance and oxidation resistance. FGM was found to be a highly favorable configuration to improve service life and stability at temperatures ~1200^0C, and at the same time without compromising the thermal barrier effect in terms of temperature gradient across the coating.

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Development of Multilayered Functionally Graded Thermal Barrier Coatings on Inconel 718 Super Alloys for Aerospace Applications

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Abstract : This paper focuses on the developmental tests on thermal barrier coated 50 x 50 x 5.2 mm (thick) aerospace alloy Inconel 718 plates. NiCrAlY (AMDRY 962) and 8YPSZ (METCO 204NS) plasma sprayable powders were used as the bond coat and top coat materials respectively. The coatings comprised of single layered as well as multilayered functionally graded configurations. The specimen underwent thermal barrier and thermal shock tests in laboratory scale burner rig test and oxidation stability tests in high temperature furnace. They were exposed to oxyacetylene flame and hot and cold face temperatures were measured by using non contact infrared thermal detector /Pt Pt- Rh thermocouple. Material characterizations of the specimen (as-sprayed and subjected to thermal tests) included Scanning Electron Microscope and X-ray diffraction (XRD) analysis. Results are presented and discussed in the light of suitability of coating configuration, thermal fatigue and spalling characteristics at temperatures in the 800 - 1400oC range. Functionally Graded Material (FGMs) configuration exhibited much superior thermal shock cycle resistance over conventional TBCs. The specimens with blended coatings in oxidation stability test were intact and exhibited no signs of formation of any defects. Functionally gradient materials results exhibit the highly superior characteristics of the multilayered systems when compared with conventional TBCs.

Keywords : Functionally Graded Materials, Thermal Barrier Coatings, Aerospace alloys.

INTRODUCTION

In order to make a metal surface more thermally insulating and to protect it from thermal degradation, thermal barrier coatings (TBCs) are applied on metal components in the form of thin (200 - 300 microns coating thickness) and thick (1-2 mm thick) coatings. Such coatings find varied functions such as in diesel, aircraft and gas turbine engines. They help to achieve improved performances, efficiency and increase the active and effective work contribution by the components [1, 2]. The thicknesses of such coatings in aircraft engines normally are in the range of 120 and 250μm and comprise of low thermal conductivity material layer. 50-120 μm inter-metallic bond coat is applied right above the pre-prepared metallic component surface to facilitate the adhesion of ceramic top coat over the metal component. The two layers of coatings i.e. bond coat and ceramic top coat are universally referred to as duplex TBCs. Plasma sprayed yttria (typically 8% Y2O3) stabilized zirconia (ZrO2) TBCs with NiAl/NiCrAlY bond coat is a well established method to fabricate TBCs [3,4]. In addition to favourable thermal insulating and expansion characteristics yttria stabilized zirconia (YSZ) possesses suitable microstructure, thermal fatigue, mechanical properties and provides protection as well from damage due to oxidation. The bond coat is an inter-metallic coating that provides relief from the damage caused by the thermal expansion mismatch between the metal substrate and ceramic over layer.

Plasma spraying is a well-researched and established method to fabricate TBCs [5]. NiCrAlY bond coats and YSZ ceramic top coat are the primary choice for applications involving aero engines. A non-transformable tetragonal phase forms during plasma spraying of YSZ coatings, which is aided by the stabilizer i.e. Yttria [9]. Plasma spray process involves rapid cooling of the sprayed powder. It is well known that the tetragonal zirconia phase is not affected by the mechanism of stress induced martensitic transformation to the monoclinic phase during cooling [8]. However, one issue related to such application is the poor adhesion (due to stress buildup in addition to oxidation) in the coatings attributed mainly to the vast difference in the expansion characteristics with temperature between the ceramic materials used as top coats and metals used in the system. The adhesion mismatch between a metal substrate and the ceramic contributes to the buildup of stresses at the interface leading to adhesive failure and sometime within inter-ceramic layers leading to cohesive failure [6].

A. Limitation of Yttria Stabilized Zirconia and Functional Gradient Materials.

Although zirconia partially stabilized with 7~8 wt% yttria (YSZ) is the current state of-the-art TBC material with thermal conductivity of ~2.12 W/m-K @ 800oC, lower thermal conductivity materials are required for future gas turbines [1]. Above 1200oC, YSZ transforms from t' phase to the tetragonal and cubic phase (t and c phases, respectively) during cooling process, and then to monoclinic phase with a volume expansion of about 3–5 vol. %, resulting in the spallation of TBCs. Additionally, at temperatures above 1200oC, YSZ layers are prone to sintering, which increases thermal conductivity and makes them less effective. The sintered and densified coatings can also reduce thermal stress and strain tolerance, which can reduce the coating's durability significantly and raise adhesion issues [7] [8]. This problem is circumvented to a large extent by processing the TBCs in different layers, comprised of gradually varying thermal conductivities. The problem arising out of thermal expansion mismatch is reduced via combination of two or more different types of coating materials to optimize the coating characteristics especially the thermal conductivities.

This method to improve the characteristics of YSZ TBCs is by formation of functionally graded materials (FGM), with a new concept of composite having gradual compositional and/or micro-structural variation over definable geometric orientations and distances [5][10]. It is known that TBCs considerably reduce the temperature of the metals substrates or parts: thereby thermal fatigue life of metal component increases and gets protection from damage mechanism involving oxidation/ corrosion. Additional benefits are expected by usage of FGM TBCs. The problem of delamination can be expected to significantly reduce by employing FGM configurations. In this system the outermost layers being ceramics, which are exposed to the high temperature harsh environment give the maximum protection. The ceramic does not end abruptly: rather being blended with bond coat, the properties of the layers below the outermost layer experience gradual compositional changes from being rich in ceramic to being rich in metal towards the component interior. The interfacial layers therefore have high fracture toughness and allow smooth transition of properties to reduce damage due to mis-matched properties between the TBC and the substrate. Thus a TBC built in FGM configuration is anticipated to be more resistant to delamination and exhibit higher durability characteristics than its counterpart i.e. a conventional TBC.

The gradient (or graded) layers can be classified based on many different parameters which depend upon the intended applications. They may be (a) microstructural (b) multilayers of metals, ceramics, polymers or (c) comprised of layers integrated with different densities/porosities etc. In duplex TBC systems, few layers of the bond coat (say NiCrAlY) are first coated (upto desired thickness) on metal components and subsequently few layers of the ceramic top coat (say YSZ) are applied. In FGM systems one method employs both the materials, the bond coat and ceramic top coat plasma spray powders co-sprayed into several layers by using a single plasma torch. FGM can also be obtained by using more than one torch at the same instance of spray coating. The challenge lies in controlling the spray parameters to form uniformly and consistently coated layers. The problem is attributed to different densities, sizes, morphologies, melting points and flowability possessed by the two kinds of spray powders. The present work is involved with formation of FGMs by using the NiCrAlY inter-metallic bond coat and 8YPSZ ceramic top coat materials in combination i.e., in form of blends.

EXPERIMENTAL

A. Materials and Methodology

The metal substrates used in this work were nickel base aerospace related super alloy (Inconel 718) composition (Ni-54.75%, Cr-17.95%, Nb+Ta-5.18%, Mo-2.98%) with a length and breadth of 50 mm X 50 mm X 5.2 mm respectively and thickness of 5.2 mm.

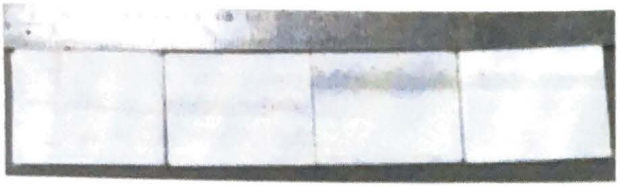

Fig. 1. Plasma spray coated TBCs on Inconel 718 Plates

Figure 1 shows typical specimen in intermediary stages of processing 50 mm X 10 mm X 5.2 mm substrates were used for oxidation stability tests. Grit blasting of metal specimen with alumina and de-greasing with solvent preceded the deposition of the bond coat followed by spray coating in FGM configurations. AMDRY 962 (Ni-22Cr-10Al-1Y,-106+52 μm) and METCO 204NS (8% Y2O3-ZrO2, -106+11 μm) plasma sprayable powders were used as the bond coat and top coat respectively. The coatings were prepared by using robot controlled 100 KW Metco Sulzer Air Plasma Spray facility. Coatings in two configurations were prepared (a) Conventional (non FGM) which comprised of a bond coat layer on the Inconel 718 plate, over which a ~ 250 micron thick top coat layer was applied and (b) FGM (non-conventional) configuration which comprised of three layers over the Inconel 718 substrate (bond coat, bond coat top coat blend and finally the top coat overlay). Typical configurations were blends of (BC and YPSZ) of 50% each, 60-40%, 25-75% etc respectively. Spray parameters which are considered during the spraying of the two types of coatings are shown in Table 1.

Table1. Spray parameters for bond coat and top coat

Parameter	NiCrAlY (Bond Coat)	%8YSZ (Top Coat)
Voltage (V)	75	70
Current (A)	400	550
Primary gas, Ar (1/min)	57	38
Secondary gas, H_2(1/min)	17	17
Power feed rate (gm/min)	45	35
Spray distance (mm)	10	10
Voltage (V)	75	70

B. Thermal Barrier Tests

The thermal barrier test involved subjecting the ceramic coated surface with a high temperature flame focused on the centre of the coated specimen, allowing the ceramic surface sufficient time (about 1 hour) to attain the intended temperature under the steady flame conditions (flame temperatures (T) varying from 1000 K up to 1800K to stabilize. Figure : 2 shows the test rig which was used for the barrier tests.

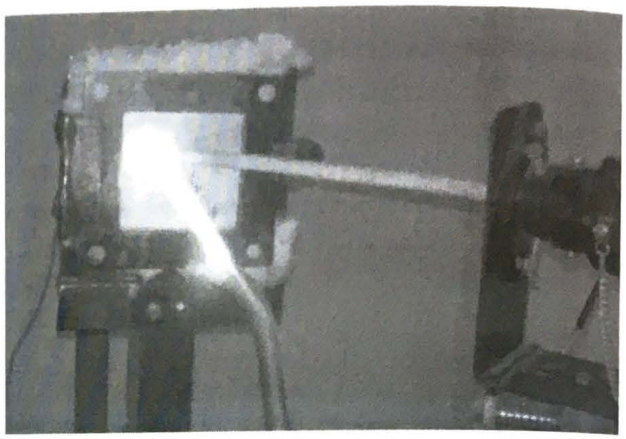

Fig. 2. Lab scale thermal (barrier and fatigue) test set-up.

C. Thermal Shock Tests

The thermal shock test involved exposing the ceramic surface to 1473K and 1673K for a pre-fixed amount of time (1 minute) and suddenly withdrawing the specimen to rapidly quench the hot ceramic surface for 1 minute. Pt-PtRh thermocouples for measurement and non contact IR thermometers were used to measure the temperatures. The numbers of such heat quench cycles were recorded to evaluate the suitability of the TBC to protect the Inconel substrate from such an extremely harsh thermal environment and subjected to materials related metrological studies.

D. Oxidation Stability Tests

Oxidation stability tests comprised of subjecting the specimen to 800oC, holding and annealing for various durations in steps of 24 hours.

RESULTS AND DISCUSSIONS

A. Thermal Barrier Test Results

The specimen (conventional and FGM) that were subjected to thermal barrier test did not show significant variation in temperature drop from each other as shown in Figure 3. That is, the temperature drop exhibited by the conventional coated substrate varied between 150 and 190° C (Hot surface temperature 1000°C – 1400°C), which was about the same exhibited by the FGM configuration.

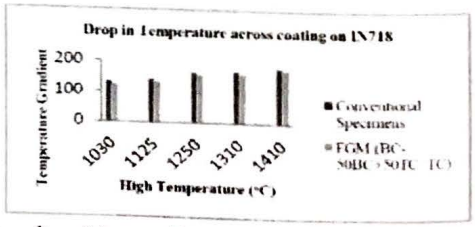

Fig.3. Results of thermal barrier test.

B. X-ray Diffraction Results

Structural phase analysis via XRD did not exhibit any significant amount of destabilization in the t-ZrO_2 phase, thereby confirming the absence of any damaging role played by the effect of the flame at 1400°C, when focused on the ceramic surface.

C. Thermal Shock Test Results

In contrast to the results obtained after thermal barrier testing, the thermal shocked test specimen exhibited significantly varied test results between the conventional and FGM configuration. The results pertain to the test when the hot face (ceramic surface) was subjected to the extremely harsh environment (flame surface temperature 1400°C). The conventional specimen failed at the end of 140 thermal shock cycles while the specimen with FGM configuration withstood more than 240 such severe cycles without failure. Failure was recorded when the topmost ceramic layer (visible to naked eye) either cracked or showed signs of degradation such as peeling off. Furthermore, the blended configuration showed significant advantage in terms of life when shock cycled between 1200°C: the conventional (non FGM configuration) TBC failed at <200 thermal shock cycles between 1200°C and ambient and in contrast the blend configuration did not fail even at >1000 cycles. These important results exhibit the highly superior characteristics of the multilayered TBCs as in FGMs. Figure 4 shows the ceramic topmost surface of the specimen at the end of thermal shock tests at 1400°C.

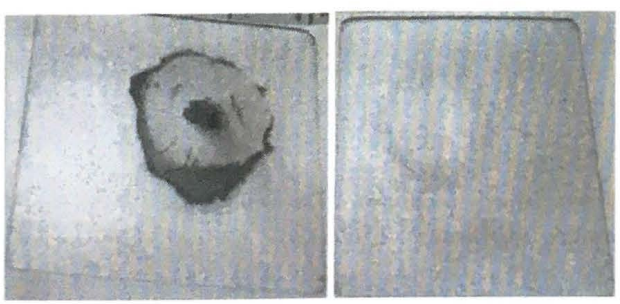

Fig. 4. Conventional specimen - failed (left) and Typical FGM configuration (right) after thermal shock cycles at 1400°C

D. Oxidation Stability Test Results

The test results obtained via thermal shock testing was amply corroborated via the oxidation stability tests (annealingat 800°C and furnace cooling to RT). The specimen coated with only bond coat and top coat (without multilayer functionally graded configuration) exhibited delamination of coating (adhesive failure) at the end of 72 hours during the oxidation stability test. The configurations with blended coatings were intact and exhibited no signs of formation of any defects. This finding confirmed the superiority of the FGM coatings when life of the coatings were considered. Figure 5 shows the photograph of specimen after 72 hours of oxidation stability test at 800oC.

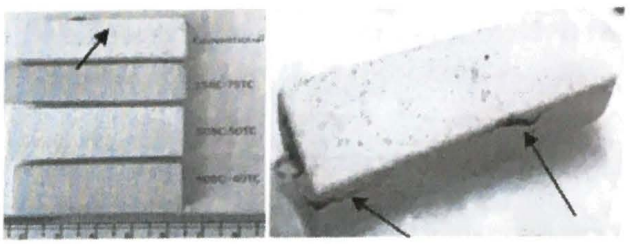

Fig. 5. Specimen after oxidation stability tests (800°C/72 hours: 24 hours anneal): Arrows show the cracks in conventionally coated specimen (non FGM configuration)

The weight gain attained by the specimen that underwent the oxidation stability test did not show any definite pattern.

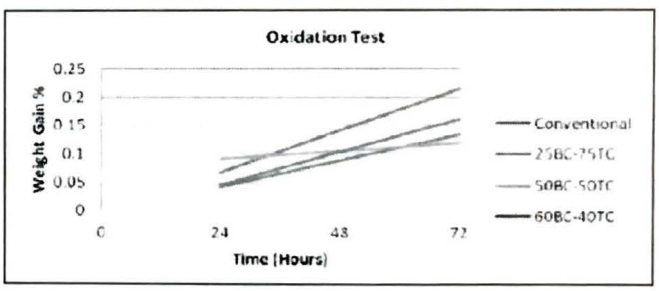

Fig. 6. Results of oxidation stability test at the end of 72 hours

However, the weights gained by all the specimen under the framework of oxidation stability test were very small and within 0.22% in a span of 72 hours. As already reported earlier in this paper, the non-FGM specimen (conventionally coated bond coat-YPSZ coating alone) failed after 72 hours of test. The graph pertaining to weight gained by the Inconel 718 specimen due to oxidization with time after 72 hours of oxidation test is shown in Figure 6.

The FGM specimen failed early in thermal shock cycling tests and in oxidation stability tests. However, the non FGM specimen did not gain significant weight during oxidation stability test and it was more or less in par with the weights gained by the FGM (blended) configurations. It may therefore be concluded that the major damage mechanism in

the non FGM (non-blended) configuration is attributable to internal stresses originated from the thermal expansion mismatch. The oxidation of the substrate did not contribute significantly to the delamination. Thus, comparing the results obtained from thermal barrier, thermal shock and oxidation stability test it is correct to summarize that coatings in FGMs configuration do not contribute towards improvement in the thermal barrier characteristics of TBCs. However, significant improvement offered by the coatings in the FGMs configurations in terms of life in service at very high temperatures is immediately noticeable.

E. SEM Analysis Results

Microstructure analysis performed on cross section metallographic specimen that has undergone thermal shock cycle tests. Figure 7 shows a typical micrograph comprised of bond coat- bond coat top coat blend - top coat configuration.

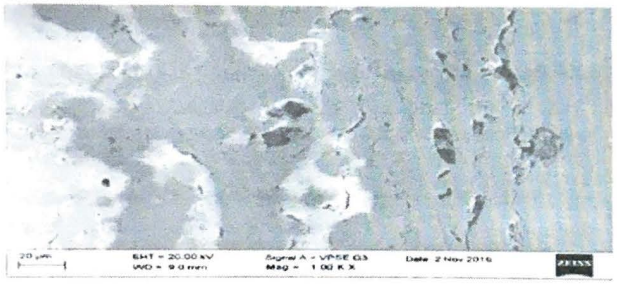

Fig. 7. SEM micrograph of FGM TBC (cross section) (as sprayed)

The SEM micrograph obtained from the FGM configuration, as expected, comprised of a thicker bond coat ceramic blended microstructure. The top coat was about 250 microns while the bond coat closest to the Inconel substrate and blended coating were about 100 microns each. As expected, the coatings in FGM configuration exhibited superior thermal shock cycle resistance which may be attributable to improved adhesion and increased inter layer adhesion strength in the FGM configuration. Large cracks developed in the conventional coating which explained the reason for the delamination of the coating. Figure 8 depicts a typical micrograph.

Fig. 8. SEM micrograph of thermal shock cycled conventional specimen (non FGM cross section) exhibiting longitudinal cohesive crack.

In contrast, the FGM configuration, at the end of 240 thermal shock cycles (between 1400°C and ambient) did not show any signs of degradation when viewed in cross section. Figure 9 shows a typical micrograph which shows a sound microstructure without failure and no delamination with some laminar cracks between the various coating layers.

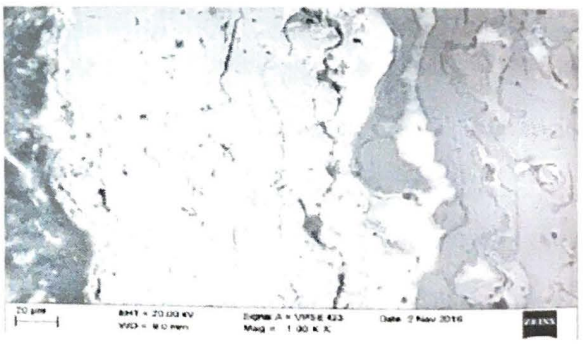

Fig. 9. SEM micrograph of thermal shock cycled FGM Configuration (cross section)

SUMMARY

Thermal barrier coatings (TBCs) fabricated from zirconia, partially stabilized with yttria over NiCrAlY bond coat were deposited by plasma spraying on aerospace alloy Inconel 718. The configurations prepared comprised of conventional (~75 microns bond coat overlaid by ~ 300 microns of top coat) and blended FGM (~75 microns bond coat overlaid by 100 microns of bond coat ceramic blended layers and finally 150 microns of ceramic top coat). All the configurations studied in the present framework of experiments (conventional and FGM) exhibited similar thermal barrier characteristics. However, the multilayered coatings with blends of the two powders (ceramic and bond coat) in Functionally Graded Material configuration exhibited

superior thermal shock cycle resistance over conventional TBCs. The improvement may be attributable to improved adhesion and increased inter layer adhesion strength in the FGM configuration. Oxidation of the substrate did not appear to be a major contributor towards the preferential failure of the coating in conventional (non FGM) configuration when compared with the coatings in FGM configuration. Thus, blended layers of intermediate coating have exhibited significant potential to provide a much longer life to the coating even when used in a very high temperature upto 1400^{0}C.

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Appendix -B

INTERNATIONAL CONFERENCES (PRESENTATIONS)

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in 1st International Conference on Manufacturing, Material Science & Engineering (ICMMSE - 2019) conducted by the Department of Mechanical Engineering, CMR Institute of Technology, Hyderabad, Telangana during 16th & 17th August, 2019.

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in 1st International Conference on Manufacturing, Material Science & Engineering (ICMMSE - 2019) conducted by the Department of Mechanical Engineering, CMR Institute of Technology, Hyderabad, Telangana during 16th & 17th August, 2019.

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in " International Conference on Composite Materials : Manufacturing, Experimental Teachniques, Modeling and Simulation " **(ICCMMEMS) 2018** held during March 15th - 17th, 2018, organized by School of Mechanical Engineering, Lovely Professional University, Punjab, India.

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Details of Course Work Completed	Month & Year of certificate Issued	February & 2018					
No of Annual presentations completed	2	Month & Year	August 2017	September 2018			
No. of department level seminars presented	1	Proof - circular & attendance (Tick): Attached / Not attached (if not attached, then it should be authenticated by HOD					
Whether monthly progress reports submitted	Yes	No ((if no, then it should be authenticated by Guide)					
Publications:							
National Conference	Nil	International Conference	6	National Journals	Nil	International Journals	7
Whether publications indexed are in these? (Tick)	Scopus/ Thomson Reuters/ Web of Science/Elsevier / ~~IEEE Xplore~~						

I. **Provide the details in the table below carefully: -**

S.No.	Name of Conference and Title of Paper	Whether your Supervisor's name included in publication?	Whether Christ (Deemed to be University) affiliation used in publication?	Provide link to view the published version of your paper available in the website, Scopus/ WOS indexed /IEEE Xplore in the website	Month & Year of publication	ISSN/ ISBN/ DOI	Plagiarism check / similarity index (from Turnitin)
1	**Conference name:** International Conference on Emerging Research in Civil, Aeronautical and Mechanical Engineering (ERCAM-2017) **Title of paper:** Development of Multilayered Functionally Graded Thermal Barrier Coatings on Inconel 718 Super Alloys for Aerospace Applications	YES	YES	Not Available Online Published in Book: McGraw Hill Education (Copy attached) Certificate Copy attached	July 2017	ISBN (13): 978-93-5260-730-3: ISBN (10): 93-5260 -730-9	NA

2	**Conference Name:** International Conference on Composite Materials: Manufacturing, Experimental Techniques, Modeling and Simulation (ICCMMEMS-2018) **Title of Paper:** Performance and Steady State Heat Transfer Analysis of Functionally Graded Thermal Barrier Coatings Systems	YES	YES	Not Available Online Certificate Copy attached	March 2018	NA	NA
3	**Conference Name:** International Conference on "Advances in Materials and Manufacturing Applications (Icon AMMA 2018) **Title of Paper:** Zirconia Based Pyrochlore Thermal Barrier Coatings	YES	YES	Not Available Online Souvenir and Certificate Copy attached	August 2018	NA	NA
4	**Conference Name:** International Conference on Materials, Manufacturing and Modelling (ICMMM 2019) **Title of Paper:** Synthesis and Studies on Partially Stabilized Zirconia and Rare-Earth Zirconate Pyrochlore Structured Multilayered Coatings	YES	YES	Not Available Online Souvenir and Certificate Copy attached	March 2019	NA	NA
5	**Conference Name:** International Conference on Manufacturing, Material Science and Engineering (ICMMSE 2019) **Title of Paper:** Influence of Atmospheric Plasma Spray Process Parameters on Crystal and Micro Structures of Pyrochlore Phase in Rare Earth Zirconate Thermal Barrier Coatings.	YES	YES	Not Available Online Souvenir and Certificate Copy attached	August 2019	NA	NA

6	**Conference Name:** International Conference on Manufacturing, Material Science and Engineering (ICMMSE 2019) **Title of Paper:** Adhesion Strength Studies on Zirconia Based Pyrochlore and Functionally Gradient Thermal Barrier Coatings	YES	YES	Not Available Online Souvenir and Certificate Copy attached	August 2019	NA	NA
Sl. No.	**Name of Journal and Title of Paper**	**Whether your Supervisor's name included in publication?**	**Whether Christ (Deemed to be University) affiliation used in publication?**	**Provide link to view the published version of your paper available in the website, Scopus/ WOS indexed /IEEE Xplore in the website**	**Month & Year of publication**	**ISSN/ ISBN/ DOI**	
1.	**Journal name:** Materials Today: Proceedings (Elsevier) **Title of paper:** Performance and Steady State Heat Transfer Analysis of Functionally Graded Thermal Barrier Coatings Systems	YES	YES	https://www.sciencedirect.com/science/article/pii/S2214785318323204 Indexed in Scopus (Elsevier) and the CPCI (Thomson Reuters, Web of Science) https://www.materialstoday.com/proceedings/	January 2018	doi.org/10.1016/j.matpr.2018.10.033	10%
2.	**Journal name:** Materials Today: Proceedings (Elsevier) **Title of paper:** Synthesis and Studies on Partially Stabilized Zirconia and Rare-Earth Zirconate Pyrochlore Structured Multilayered Coatings	YES	YES	**In- print** **(Accepted for Publication)** **Date: 14 February 2019** **Mail copy attached** Indexed in Scopus (Elsevier) and the CPCI (Thomson Reuters, Web of Science) https://www.materialstoday.com/proceedings/	Not Published yet		8%
3.	**Journal Name:** Frontiers in Advanced Materials Research **Title of Paper:** Thermal Shock and Oxidation Stability Tests to Grade Plasma Sprayed Functionally Gradient Thermal Barrier Coatings	YES	YES	https://www.sietjournals.com/index.php/famr/article/view/8 **Non- Scopus Indexed**	May 2019	DOI: 10.26524/famr1911	9%

4.	**Journal Name:** Materials Today: Proceedings (Elsevier) **Title of Paper:** Adhesion Strength Studies on Zirconia Based Pyrochlore and Functionally Gradient Thermal Barrier Coatings	YES	YES	https://www.sciencedirect.com/science/article/pii/S2214785319330263 Indexed in Scopus (Elsevier) and the CPCI (Thomson Reuters, Web of Science) https://www.materialstoday.com/proceedings/	December 2019	doi.org/10.1016/j.matpr.2019.07.735	11%
5.	**Journal Name:** Materials Today: Proceedings (Elsevier) **Title of Paper:** Influence of Atmospheric Plasma Spray Process Parameters on Crystal and Micro Structures of Pyrochlore Phase in Rare Earth Zirconate Thermal Barrier Coatings	YES	YES	https://www.sciencedirect.com/science/article/pii/S2214785319330585 Indexed in Scopus (Elsevier) and the CPCI (Thomson Reuters, Web of Science) https://www.materialstoday.com/proceedings/	December 2019	doi.org/10.1016/j.matpr.2019.07.760	12%
6.	**Journal Name:** Institute of Physics (IOP) Conference Series Materials Science and Engineering **Title of Paper:** Zirconia Based Pyrochlore Thermal Barrier Coatings	YES	YES	https://iopscience.iop.org/article/10.1088/1757-899X/577/1/012099 Indexed in Scopus (Elsevier) and the CPCI (Thomson Reuters, Web of Science) https://conferenceseries.iop.org/content/quick_links/Abstracted%20In	December 2019	d.i.o 10.1088/1757-899X/577/1/012099	9%
7.	**Journal Name:** *International Journal of Advanced Mechanical Engineering (IJAME)* **Title of Paper:** Systematic Review of the Suitability and Utility of Thermal Barrier Coatings for Enhancement of Performance of Auto Engines.	YES	YES	**Under Review** Acknowledgment email copy attached Date: 11 June 2019 Scopus indexed journal http://journal.ump.edu.my/ijame/indexing	Not Published yet	ISSN: 2229-8649	7%

Saw the Not Published Review Paper on Scopus site

8.	**Journal Name – Scopus Indexed (to be decided)** **Title of Paper:** Residual Stresses Analysis: A Non-Destructive Method to Assess the Physical Condition of Thermally Stressed TBCs	YES	YES	Ready for Submission	Not Applicable	Not Applicable	Not Applicable

Note if any, on publications made: 5 papers published (or accepted for printing) in, Scopus/ WOS indexed journals, 1 printed in non-Scopus journal, 1 ready for submission
Citations, if any: Few papers have been recommended for reading

II. Confirmation:

1. The above information has been filled in concurrence with my research supervisor.
2. The PDF copies of **published version of papers** are also attached.

Signature of Scholar with date: P. Kavitha 13/1/2020

Verified by PhD office 29/01/2020

REMARKS BY THE RESEARCH CENTRE AUTHORITY (FOR OFFICE USE ONLY): (to be filled)

Dr S Suganthi, Research Coordinator
Name and Signature of Verifier

Date: 29.01.2020